



Novel Zeolitic Imidazolate Framework/Polymer Membranes for Hydrogen Separations in Coal Processing

Inga H. Musselman, John P. Ferraris, Kenneth J. Balkus, Jr.

Department of Chemistry, The University of Texas at Dallas

**UCR/HBCU Contractors Review Conference
Pittsburgh, PA
June 2-3, 2010**



DE-NT0007636

Dr. John P. Ferraris, Professor

Ph.D., Organic Chemistry
The Johns Hopkins University

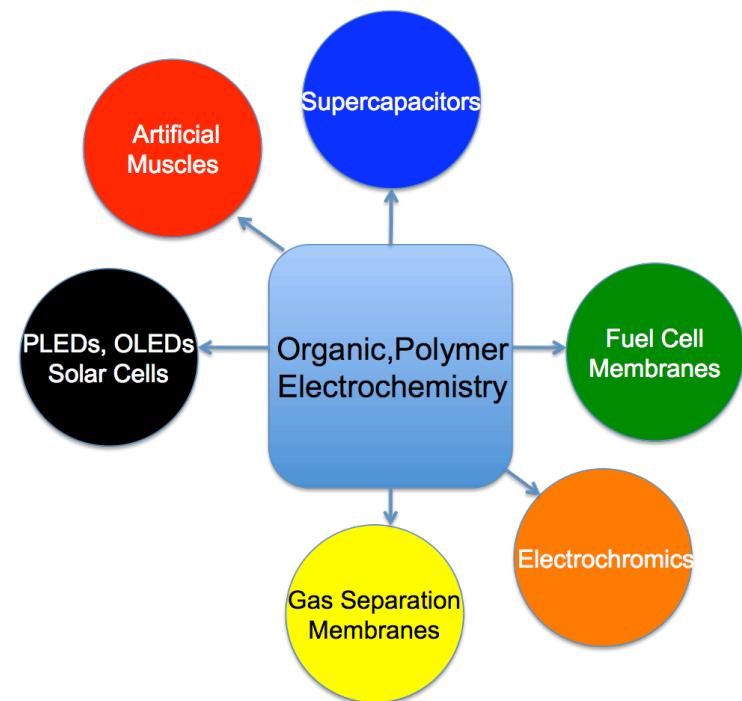


Areas of expertise

- **Semiconducting polymers**
- **Fuel cells**
- **Membrane separations**
- **Organic/polymeric solar cells**
- **Supercapacitors**

ferraris@utdallas.edu

www.utdallas.edu/~ferraris



Dr. Kenneth J. Balkus, Jr., Professor

Ph.D. Inorganic Chemistry, University of Florida

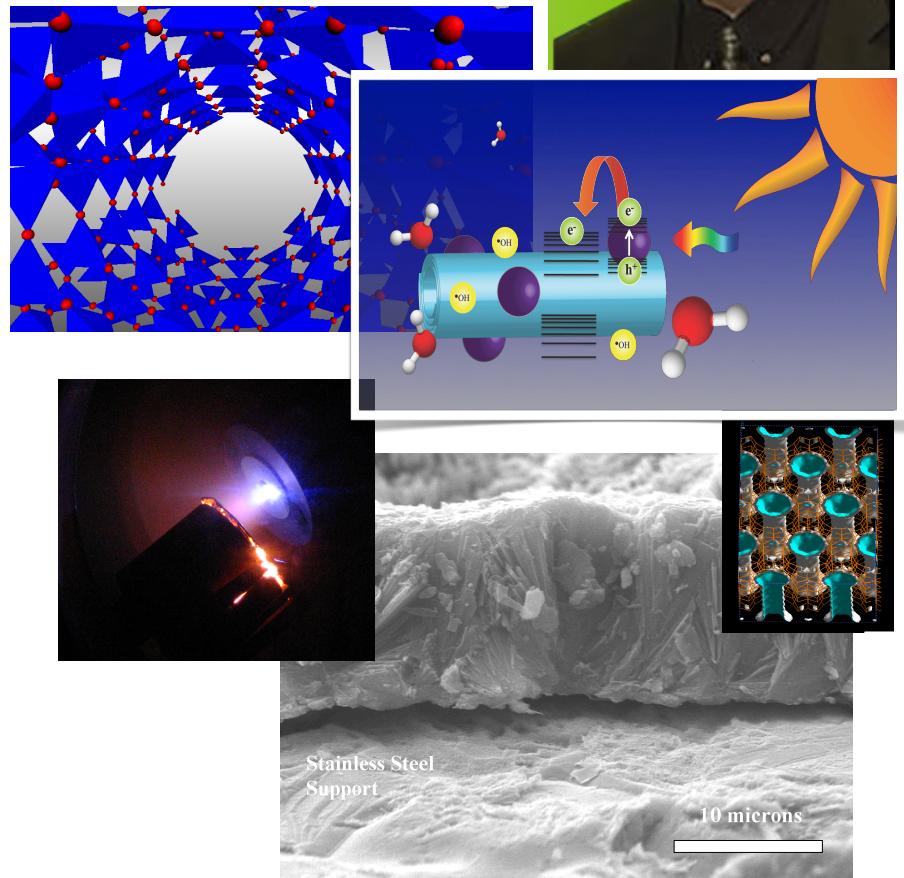


Areas of expertise

- Nanoporous materials
- Catalysis
- Membranes
- Alternative energy

balkus@utdallas.edu

www.utdallas.edu/~balkus



Dr. Inga H. Musselman, Professor

Ph.D. Analytical Chemistry, U. of North Carolina

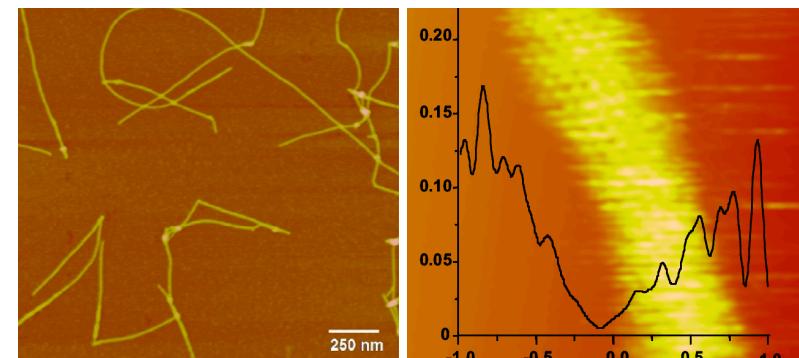
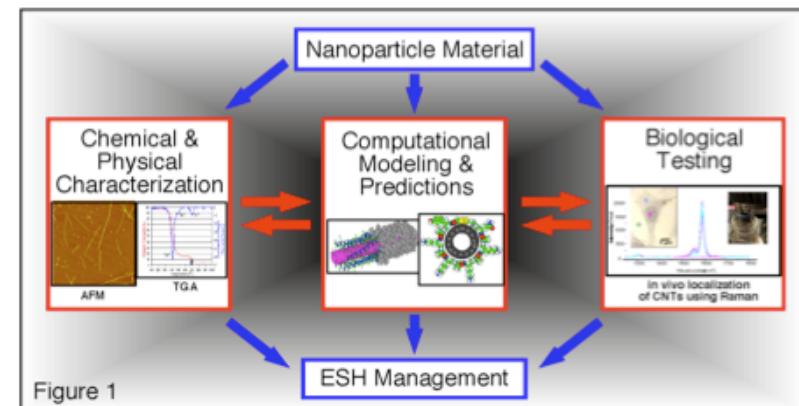
imusselm@utdallas.edu

<http://www.utdallas.edu/chemistry/faculty/musselman.html>



Areas of expertise

- Alternative energy
gas separations
fuel cells
- Bionanotechnology
properties of SWNTs
nanoparticle toxicity
targeted tumor ablation
TEM 3-D tomography



I. Introduction to H₂ separations

II. Mixed-matrix membranes (MMMs)

III. UT-Dallas project

- i. High performance polymers
- ii. Metal-Organic Frameworks (MOFs) and Zeolitic Imidazolate Frameworks (ZIFs)
- iii. Selected ZIF MMMs
- iv. High temperature-high pressure permeameter

IV. Results to date

V. Future work



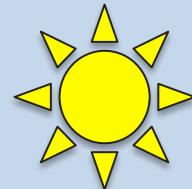
Introduction to Hydrogen Separations

Hydrogen Sources

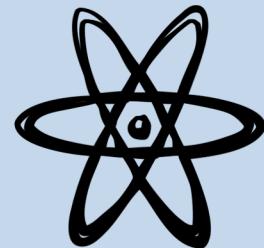
Biomass Fuels



Barks,
Mulches,
Agricultural
residues, etc.



Hydro
Wind
Solar
Geothermal

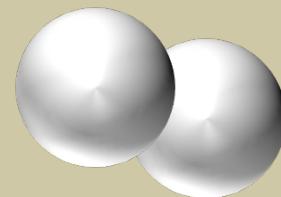


Nuclear



Fossil
Fuels

H₂ Production

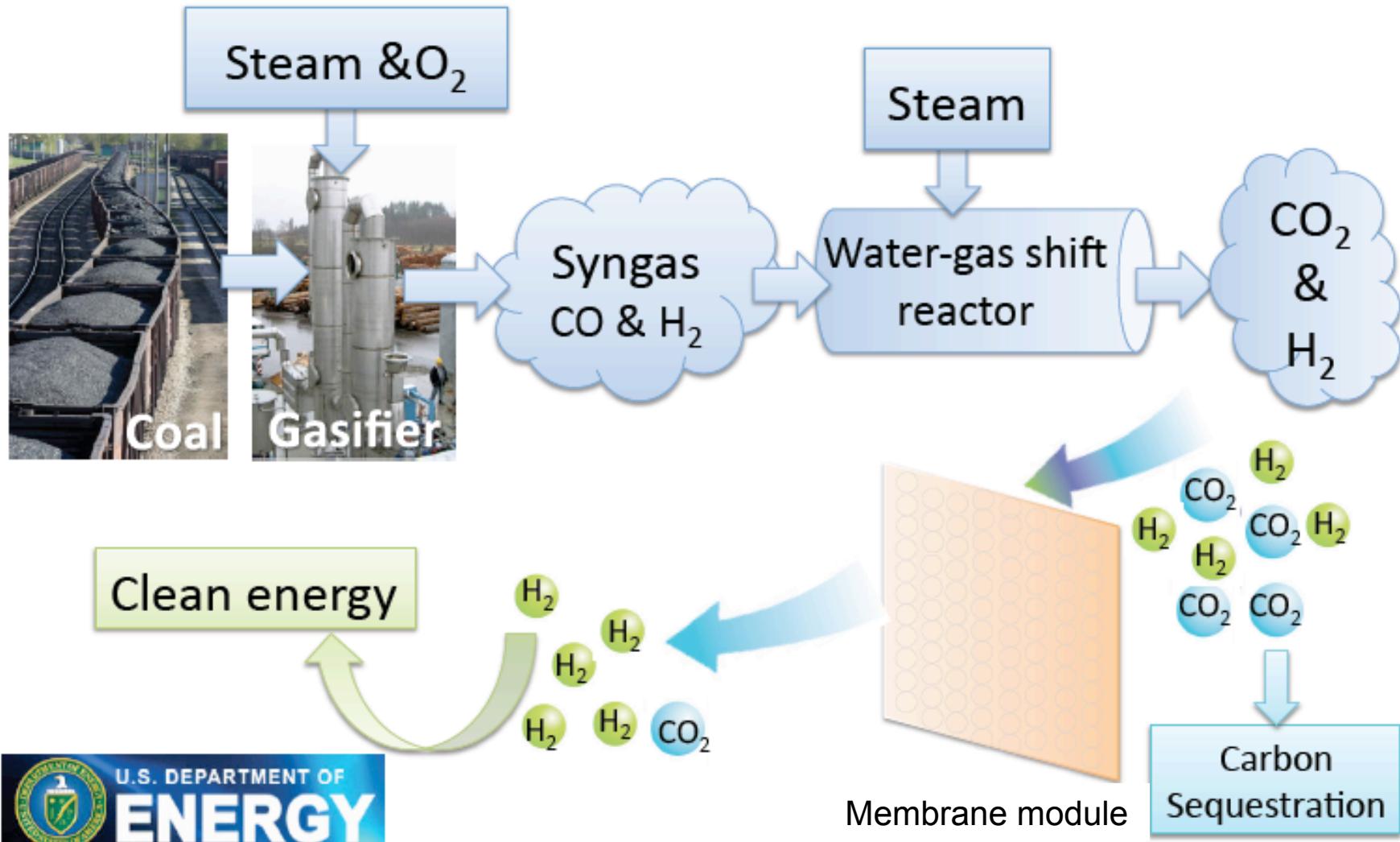


H₂

COAL

- An abundant natural resource in the U.S. (250-year supply)
- Currently providing only 19% of the U.S. production of H₂

Coal Gasification



Hydrogen separation and production technology

- Hydrogen flux: 300 SCFH/ft² @ 100 psi ΔP H₂ partial pressure
- Temperature: 250 to 500 °C
- Pressure performance: ΔP 800 to 1000 psi
- Sulfur tolerance: >100 ppm
- CO tolerance
- Water Gas Shift (WGS) activity
- Hydrogen purity: 99.99%

H₂/CO₂ Separation



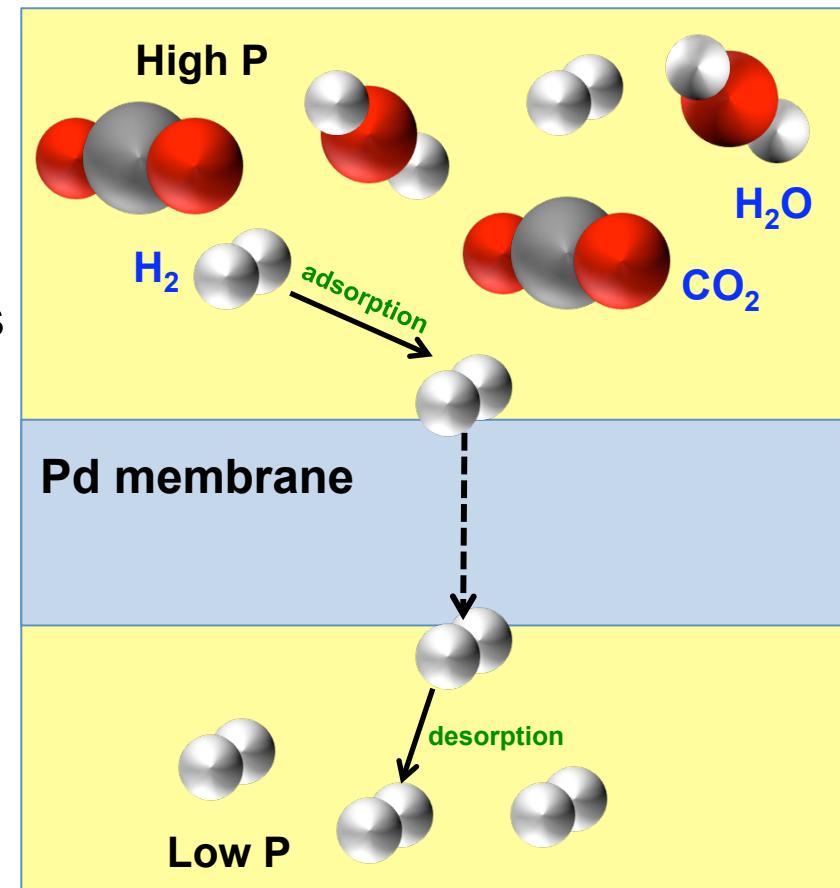
Current membranes for H₂/CO₂ separation are based on dense Pd or Pd-coated ceramic membranes.

Advantages:

- ◆ Extremely high H₂/CO₂ selectivity
- ◆ Reasonable H₂ flux at high pressures

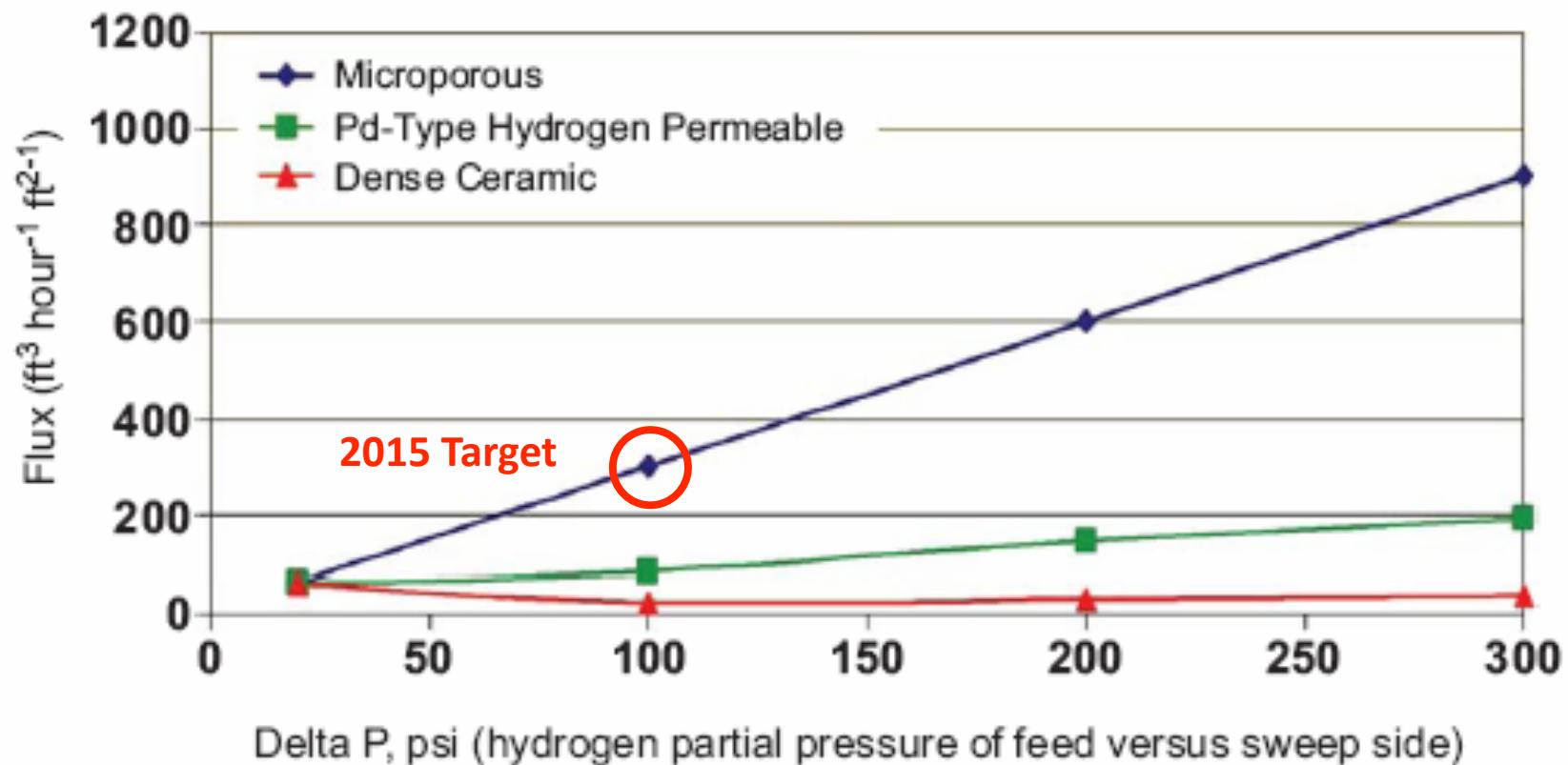
Disadvantages:

- ◆ Embrittlement
- ◆ H₂S poisoning
- ◆ Cost
- ◆ Large carbon foot print!



Effect of ΔP on H_2 Flux

Microporous membranes show the potential to achieve high H_2 fluxes at low ΔP [1]



[1] Hydrogen from coal program: Research, development, and demonstration plan, U. S. DOE, 2009

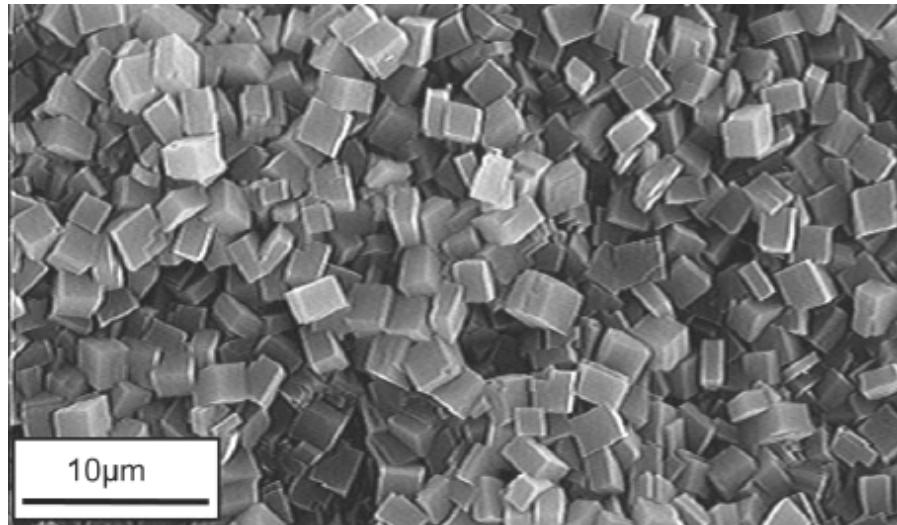
Inorganic Membranes

Advantages:

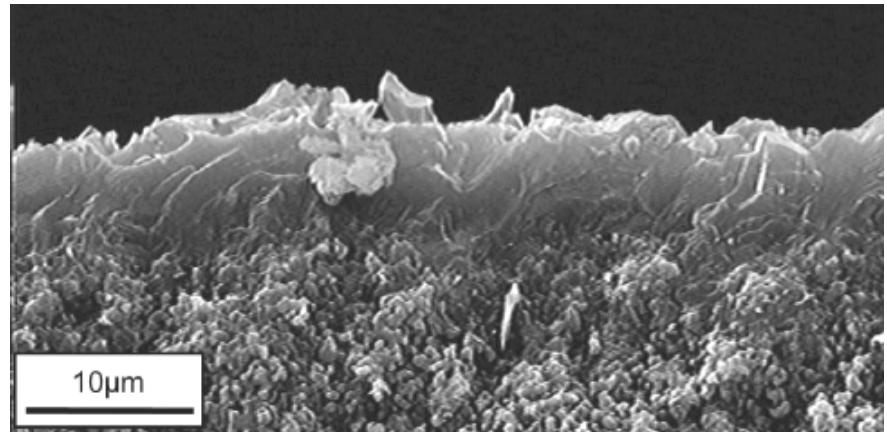
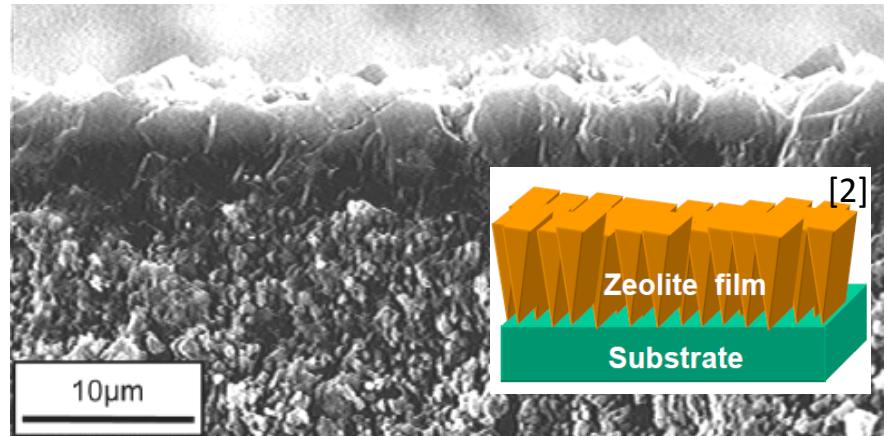
- ◆ High flux (5-10 fold higher P)
- ◆ Good selectivity

Disadvantages:

- ◆ High manufacturing costs
- ◆ Low mechanical resistance
- ◆ Limited to flat or tubular membranes

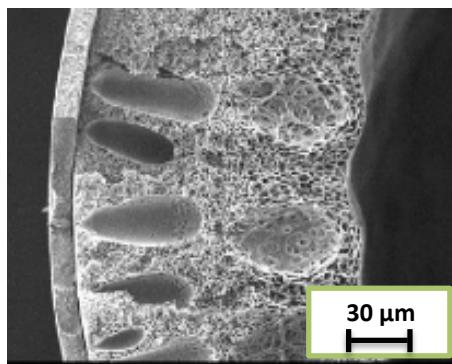
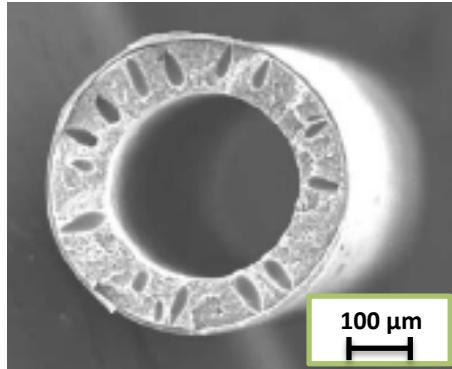


SEM of the surface of SAPO-34 membrane [1]



SEM of the cross-section of a SAPO-34 membrane: one synthesis layer (top) and two synthesis layers (bottom) [1]

Polymer Membranes



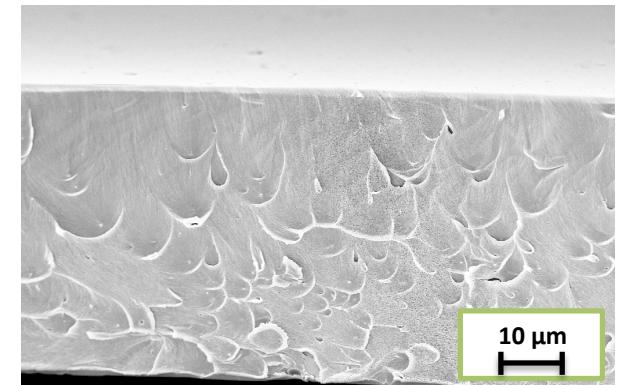
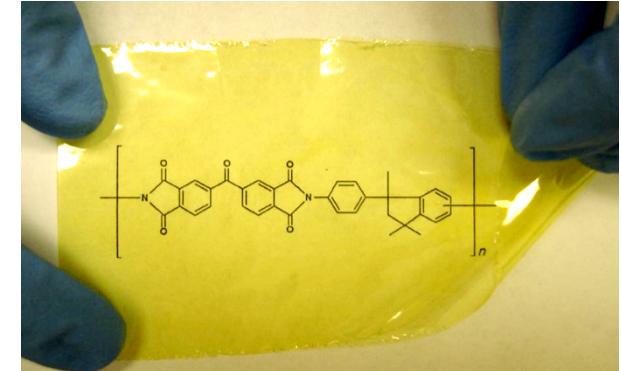
SEM of the cross-section of Matrimid®/polyethersulfone dual-layer hollow fiber membrane [1]

Advantages:

- ◆ Low manufacturing costs
- ◆ High mechanical resistance

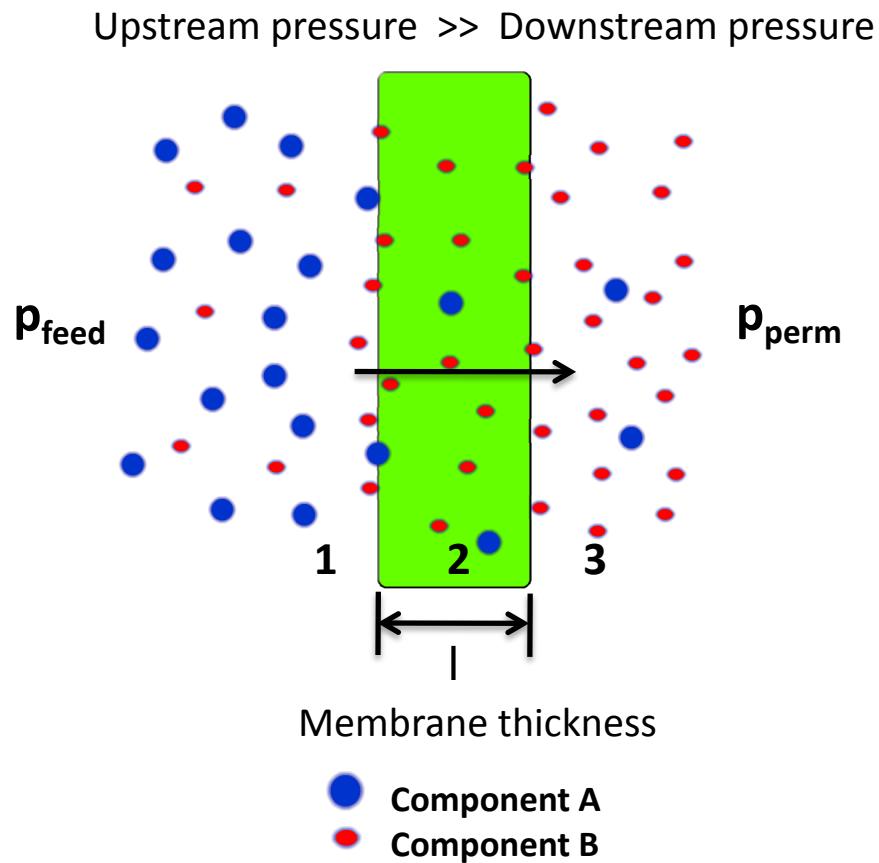
Disadvantages:

- ◆ Low flux
- ◆ Low selectivity
- ◆ For gases with low T_c (H_2), diffusivity more important than solubility



Optical image (top) and SEM of the cross-section (bottom) of a flat Matrimid® membrane

Gas Transport in Polymers



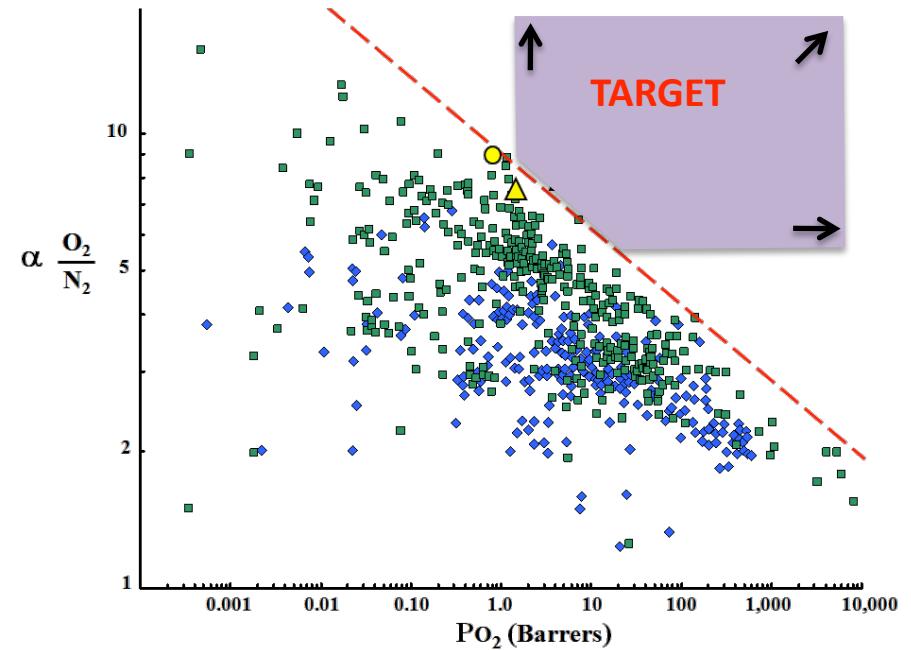
1. Sorption on upstream side
2. Diffusion across partial pressure gradient
3. Desorption on downstream side

- Permeability of A = $P_A = D_A S_A$

where S_A = Solubility coefficient of A

D_A = Diffusion coefficient of A

- Selectivity = $\alpha_{A/B} = \frac{P_A}{P_B} = \left(\frac{D_A}{D_B} \right) \left(\frac{S_A}{S_B} \right)$



Robeson, L. M., *J. Membr. Sci.* **1991**, 62, 165



Mixed-Matrix Membranes (MMMs)

Mixed-Matrix Membranes

(Nanoparticle-polymer composites)

Advantages:

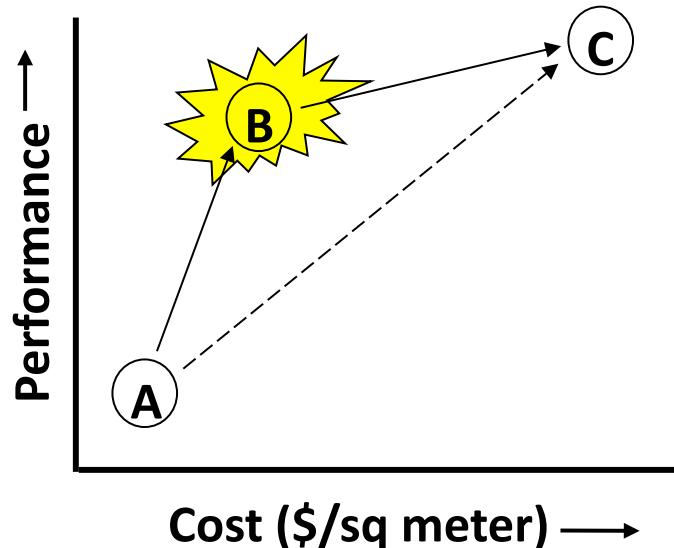
- ◆ Low manufacturing costs
- ◆ Superior separation of inorganic materials with processability of polymeric materials
- ◆ Possibility to test materials that would not form membranes
- ◆ High loadings may be necessary to overcome polymer permeation properties

Historical Disadvantage:

- ◆ Embrittlement limits loading of inorganic material (40 wt% zeolite)

Costs of Membrane Materials

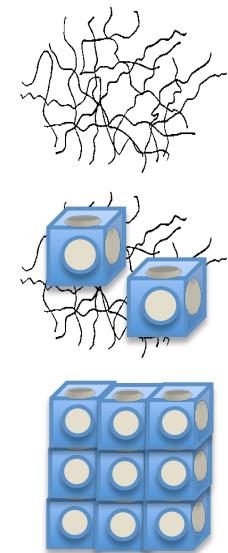
Revolutionary ($A \rightarrow C$) vs. Evolutionary ($A \rightarrow B \rightarrow C$) Strategies



A current organic polymers

B mixed-matrix hybrids

C pure inorganics or carbons

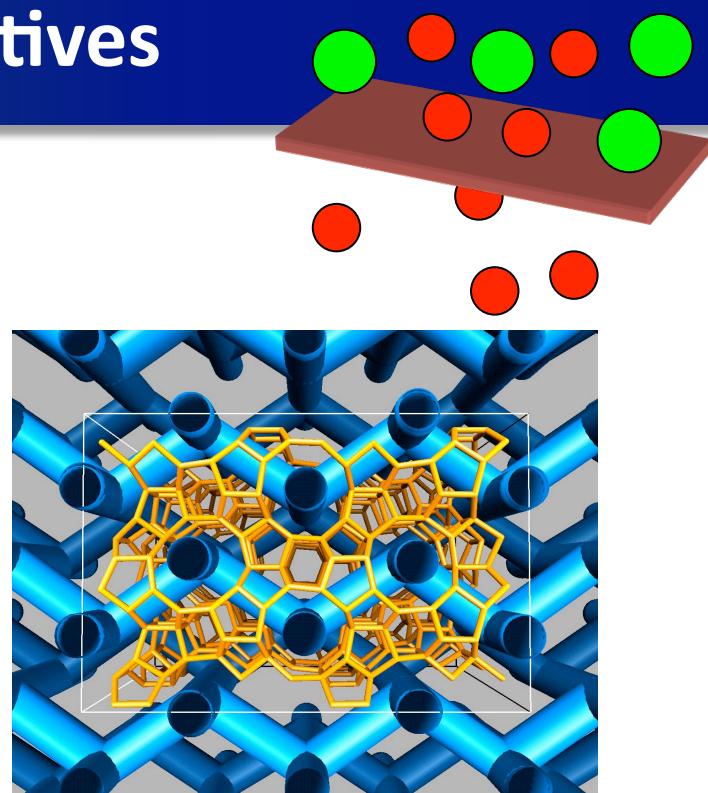


Organic-inorganic hybrids may maintain low cost of current organic polymers and approach performance of inorganics (\$2-\$10/sq ft).
2015 DOE Target <\$100/sq ft

Typical Additives

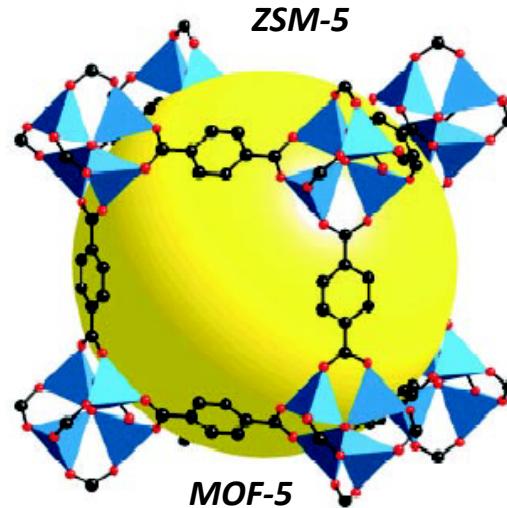
	Kinetic Diameter	Critical Temp.
N ₂	3.64 Å	-147 °C
O ₂	3.46 Å	-118.4 °C
CH ₄	3.8 Å	-82.1 °C
CO ₂	3.3 Å	31 °C
H ₂	2.89 Å	-232.6 °C

Zeolites – uniform pores, stable



Carbon – high surface area but non-uniform pores

Metal-organic frameworks – uniform pores, very high surface area (8000 m²/g)



New Paradigm for MMMs

OLD Approach

“Mixed matrix membranes allows membrane selectivity to be enhanced through gas solubility optimization.”

Santi Kulprathipanja Membrane Technology 144 (2002) 9-12

i.e. the effort has largely been directed at enhancing the properties of the polymer by dispersing nanoporous additives

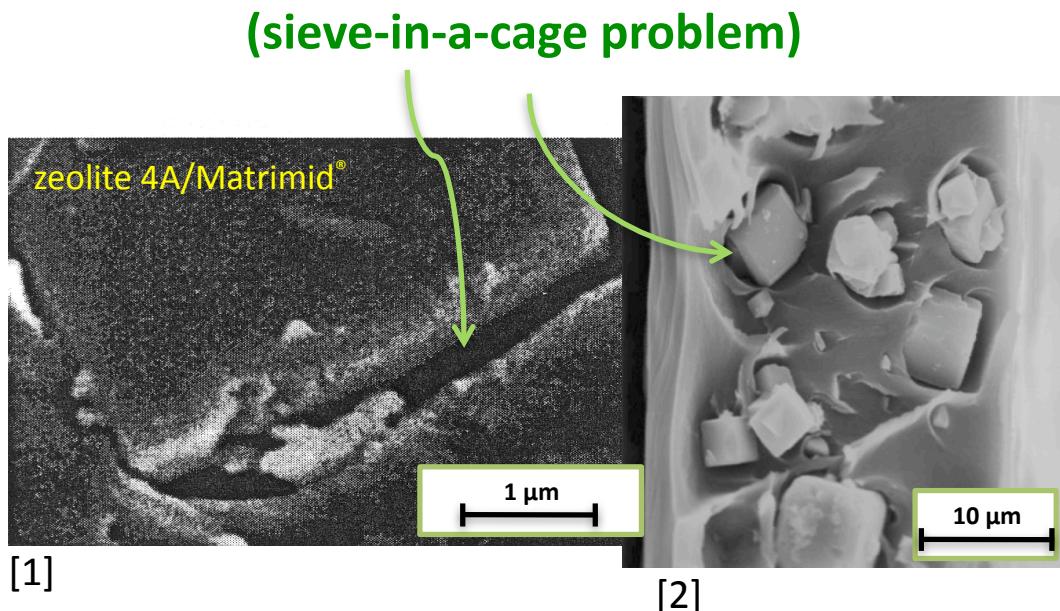
NEW Approach

Mixed matrix membranes where the polymer acts as a binder such that the permeation properties are determined by diffusion through the nanoporous additive.

This requires high (>50%) loadings.

H_2/CO_2 separation: target H_2 sieving (pore aperture) and increased diffusivity (porosity) performed by the additive

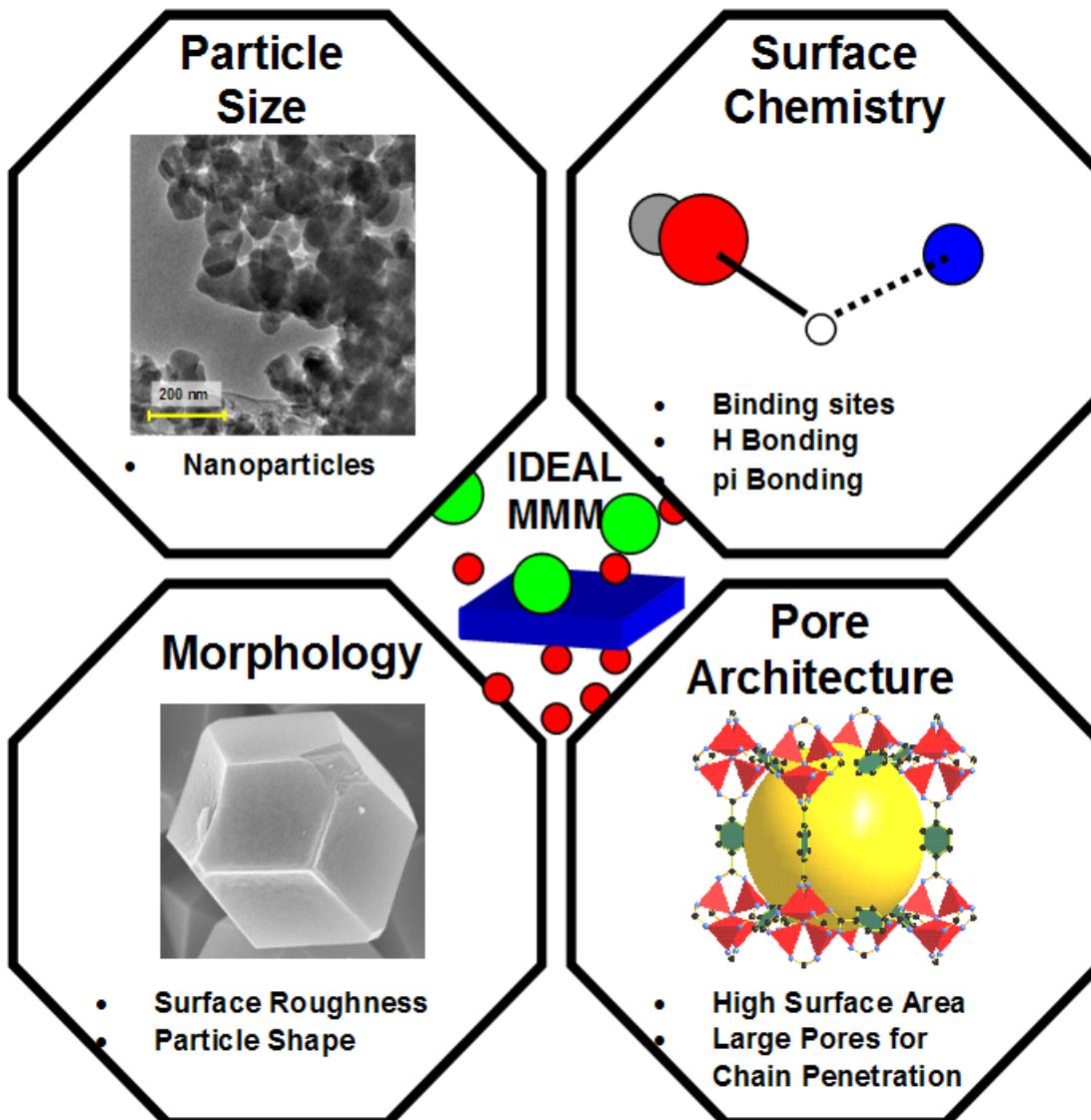
- ◆ *Challenges with inorganic–organic interface:* new materials needed for improved compatibility



Ideal MMM

- ◆ High additive loadings (>50 wt%)
- ◆ Processable at high loadings
- ◆ Membrane transport properties approach the additive properties

Strategies for Improving Interfaces



UTD project objectives (DE-NT0007636)

- Prepare novel MMMs based on polymer composites with nanoparticles of zeolitic imidazolate frameworks (ZIFs)
 - Synthesis of high performance polymers
 - Synthesis of ZIFs
 - Fabrication of MMMs
- Evaluate MMMs for separations important to coal gasification (e.g. H₂, CO, O₂, CO₂)
- Test performance of MMMs under operating conditions defined by 2015 DOE targets
 - Construction of high pressure-high temperature permeameter

Material Requirements

Polymer

- Stable above 300 °C
- Processable
- Compatible with hollow fiber processing
- Film-forming
- Separation properties close to upper bound (H_2/CO_2 separation)
- Low swelling
- Stability to H_2O (steam), CO, and H_2S

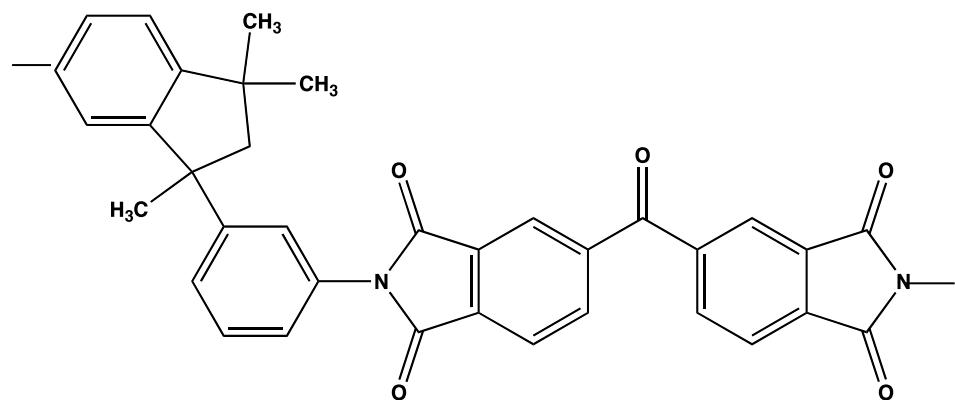
Inorganic Additive

- Stable above 300 °C
- Stability to H_2O (steam), CO, and H_2S
- Fabricated as nanoparticles
- Controlled pore size
- High surface area
- Strong interaction with polymer

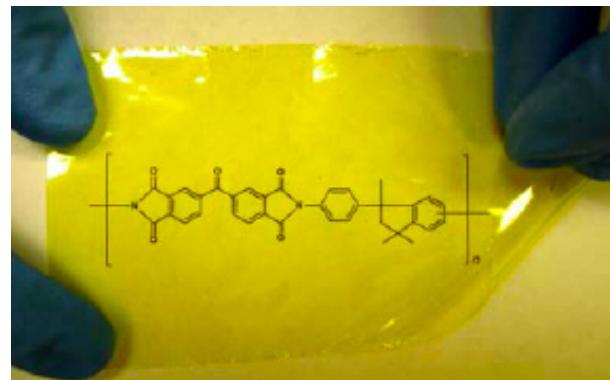


High Performance Polymers: Commercial and Synthesized at UTD

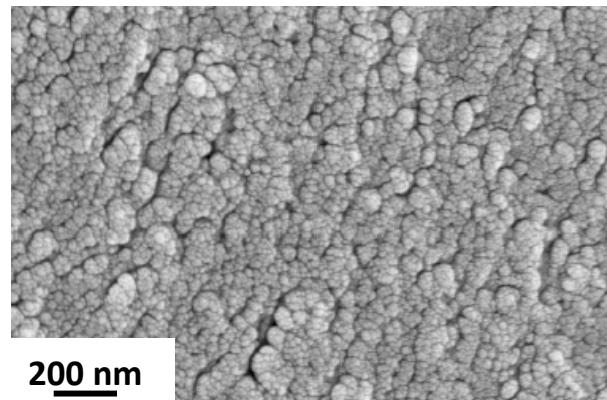
Matrimid®



- Commercially available
- Polyimide
- $T_g = 338 \text{ }^\circ\text{C}$



optical image



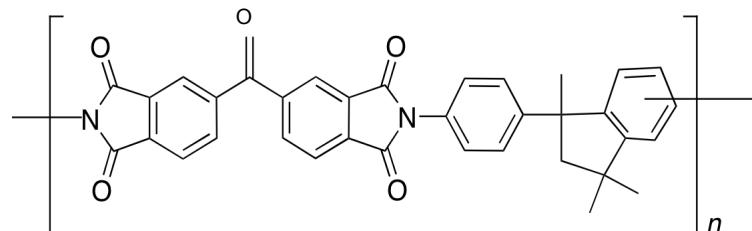
SEM image

EDA cross-linked Matrimid®

- EDA (ethylenediamine)



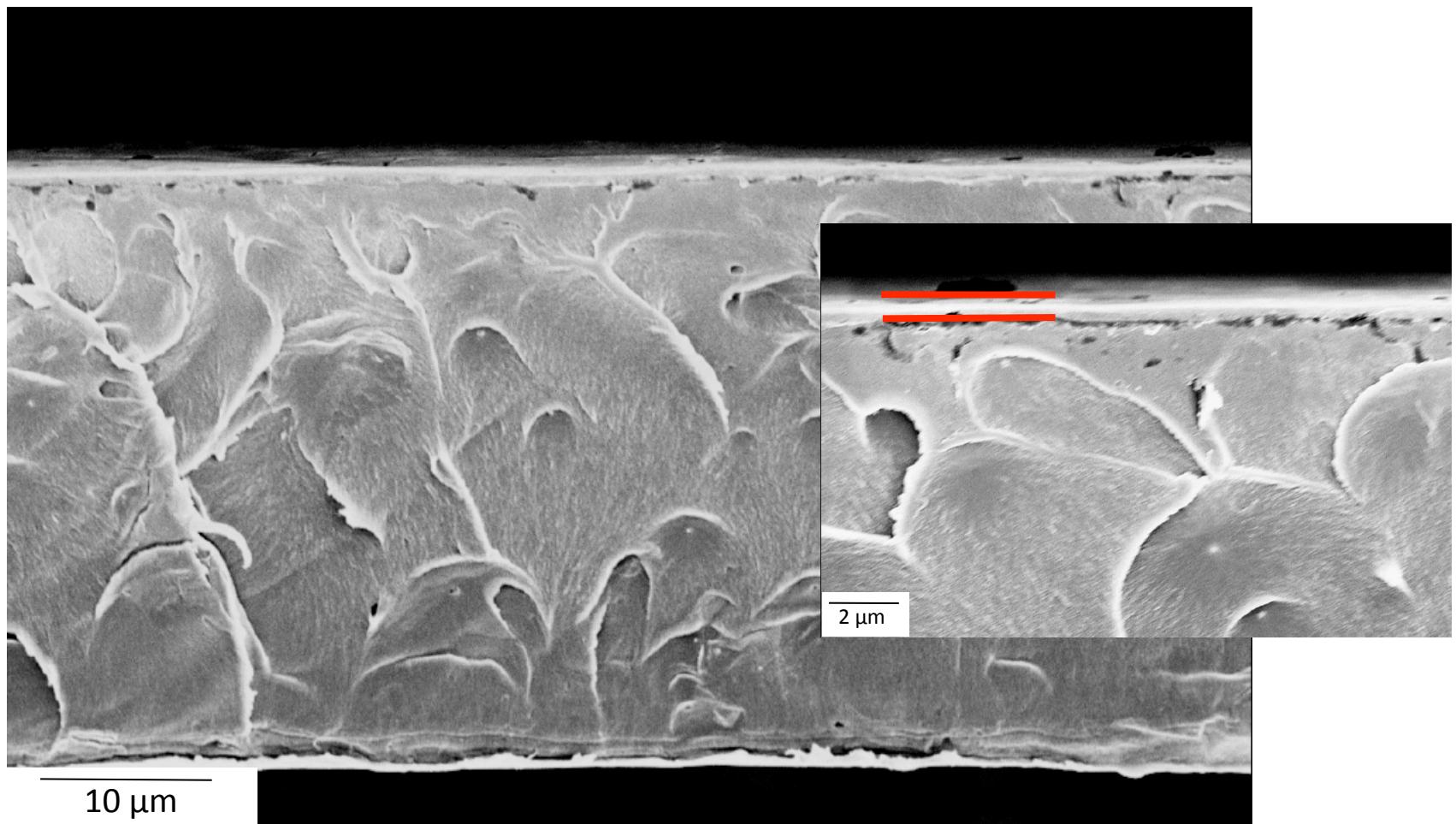
- Matrimid®



- Modify the outer surface of the membrane

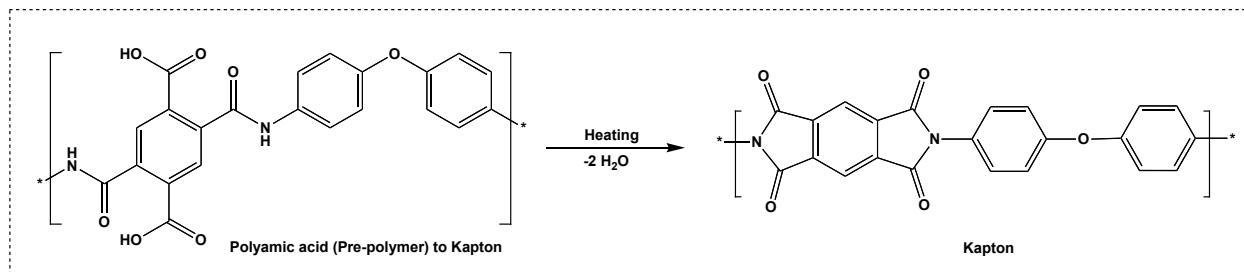


Matrimid® cross-linked with EDA for 3 h showing skin



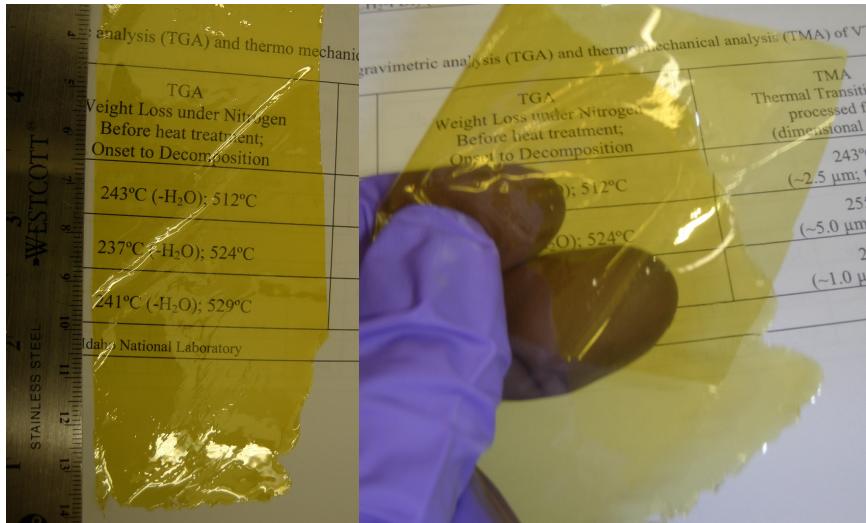
VTEC PI-1388 polyimide

**VTEC PI-1388 similar to
Kapton® in structure
 $T_g > 500 \text{ }^\circ\text{C}$**



Good mechanical stability and film formation

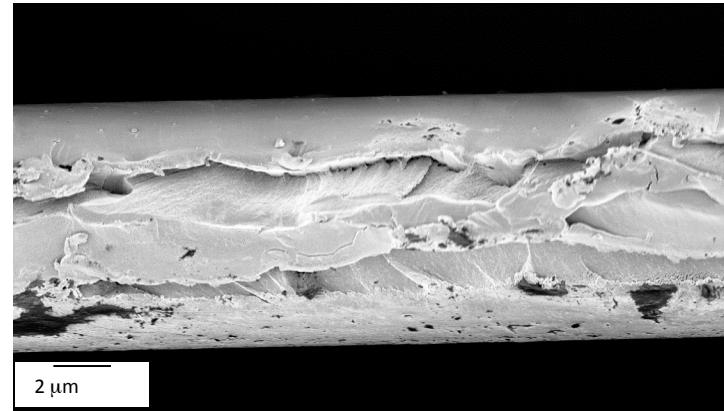
Optical image of VTEC PI-1388 cast from DMAc



Prepared from 20 wt% solution in NMP (PBI Performance, Inc.)

Thermally stable up to 529 °C

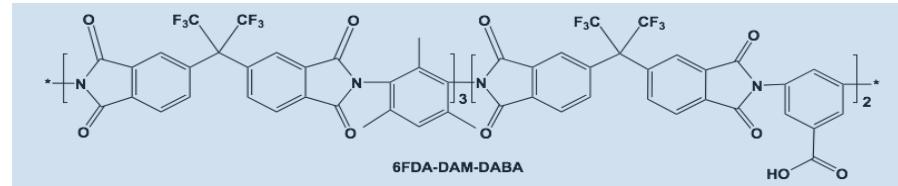
SEM image of a cross-section of VTEC PI-1388 cast from DMAc



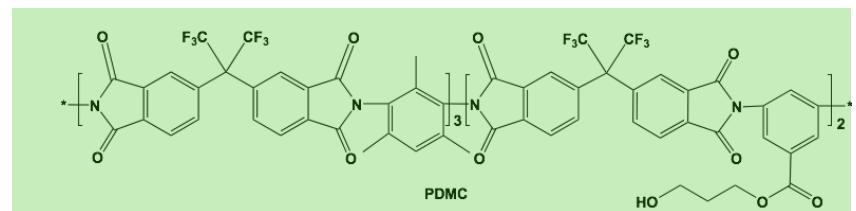
Cross-linked propane diol monoester (CPDM)

- Cross-linked polyimide containing hexafluoroisopropylidene functionality in the back bone
- Synthesized in 3 steps

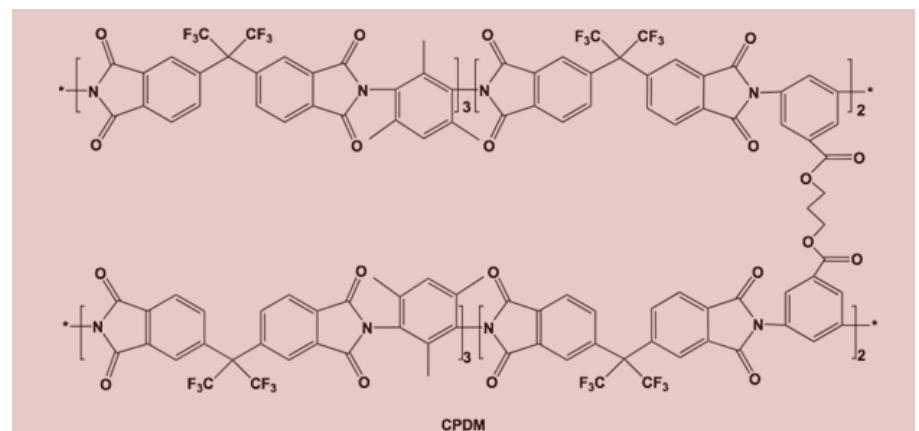
1. Synthesis of 6FDA-DAM-DABA polymer using the 3 monomers
6FDA, DAM, and DABA

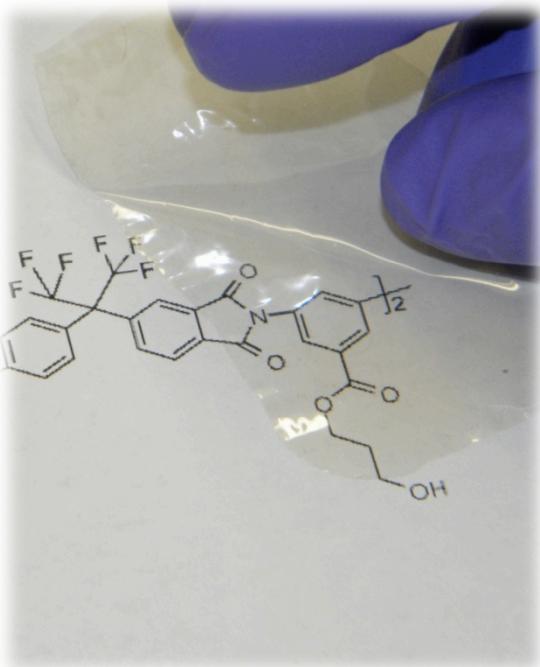


2. Esterification using propanediol

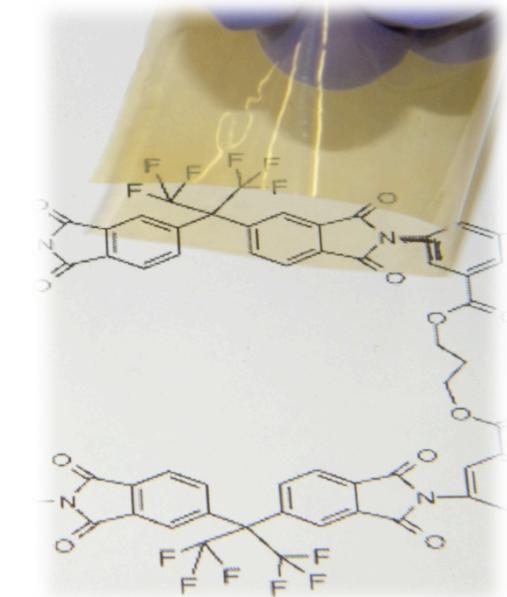
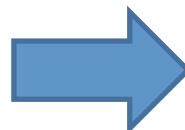


3. Cross-linked
 $T_g = 360 \text{ }^\circ\text{C}$

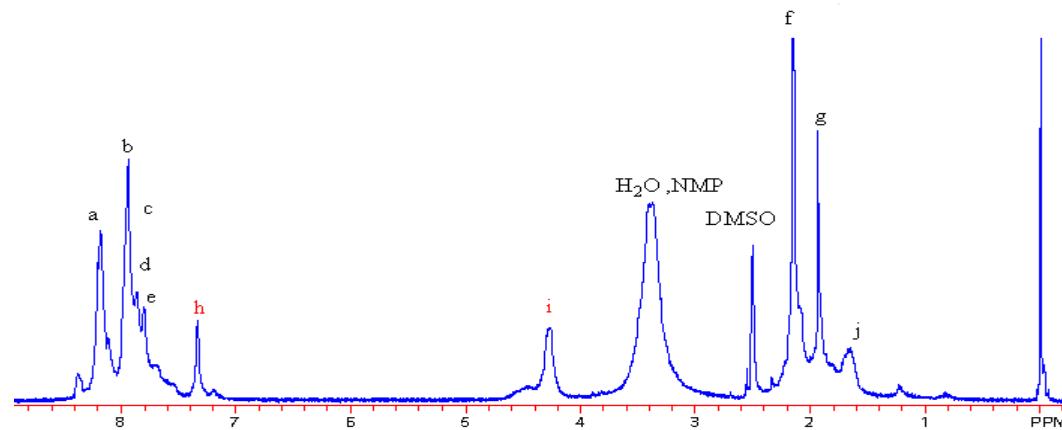




Cross-linked
by heating at 285 °C
for 1 d

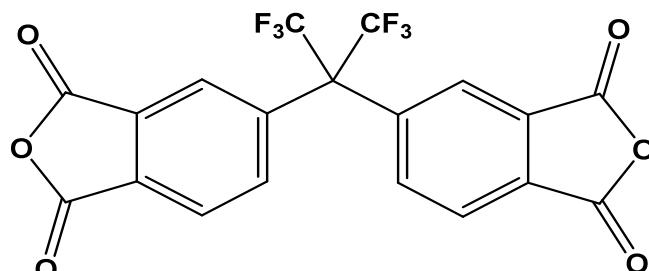


¹H NMR of PDMC



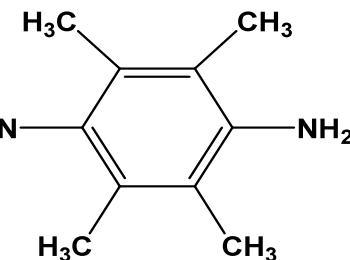
6FDA-durene

- Polyimide containing hexafluoroisopropylidene functionality in the backbone,
 $T_g = 424 \text{ }^\circ\text{C}$
- Polymerization of 6FDA and durene-diamine through chemical imidization



6FDA

1:1 monomer mixture in NMP
(20 wt%)
Stir at RT for 26 h under N_2 purge

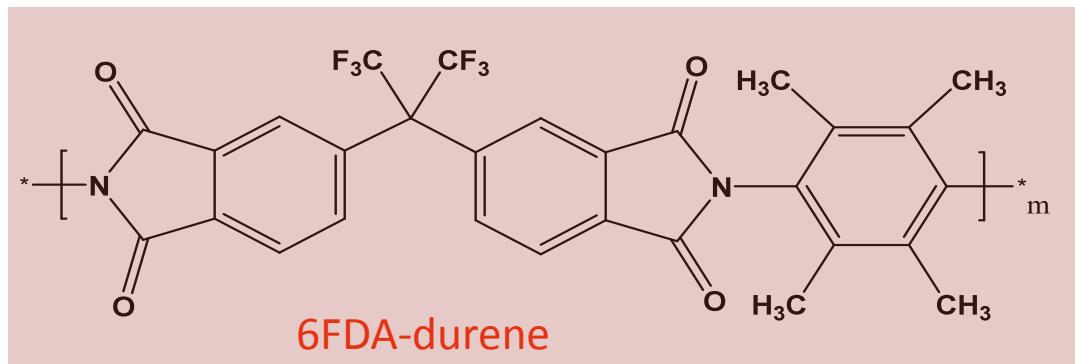


Durene diamine

Add 1:1 TEA: AcAn
4x moles of 6FDA
stir at RT for 30 h

6FDA-durene
 $\alpha \text{ H}_2/\text{CO}_2 = 1$

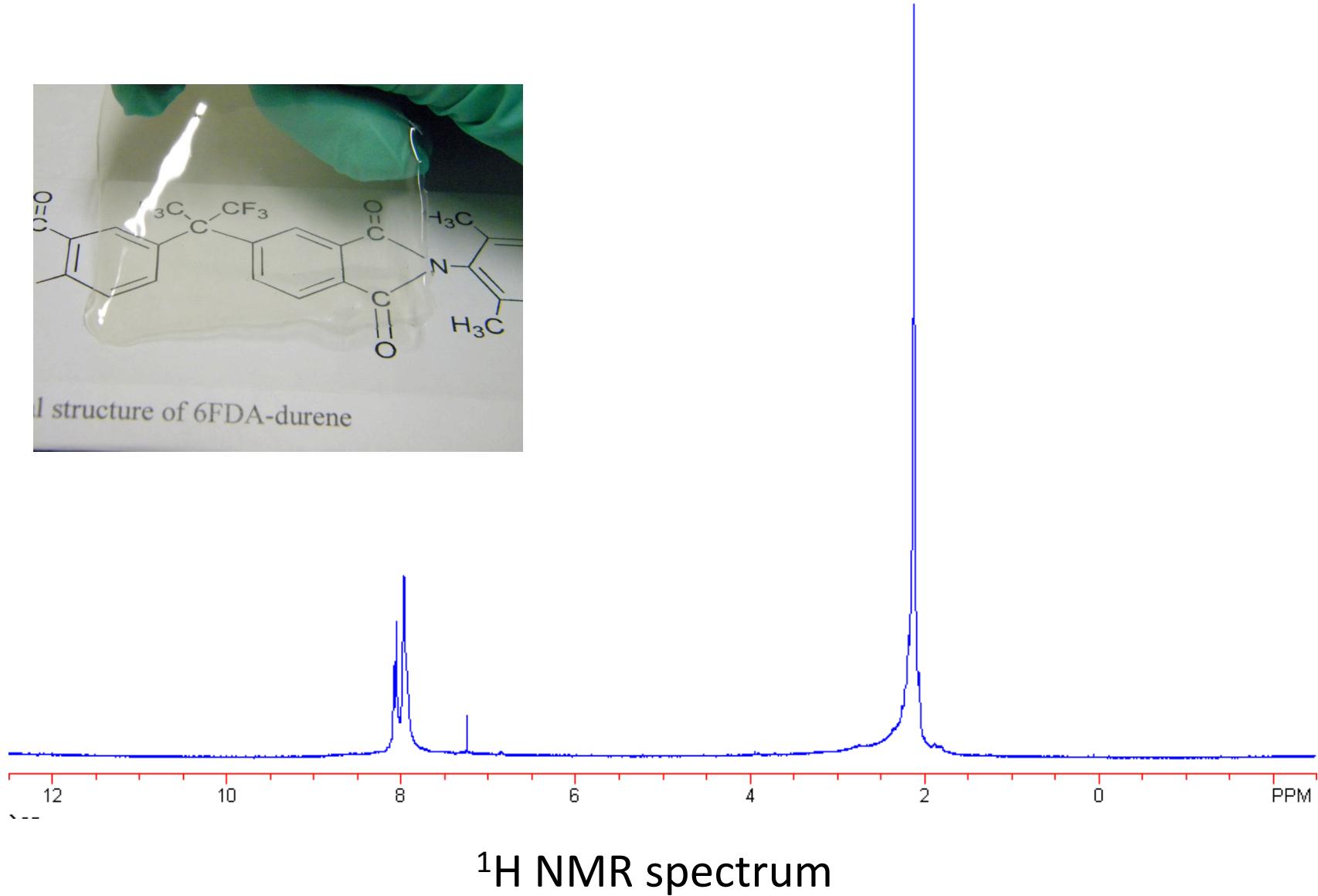
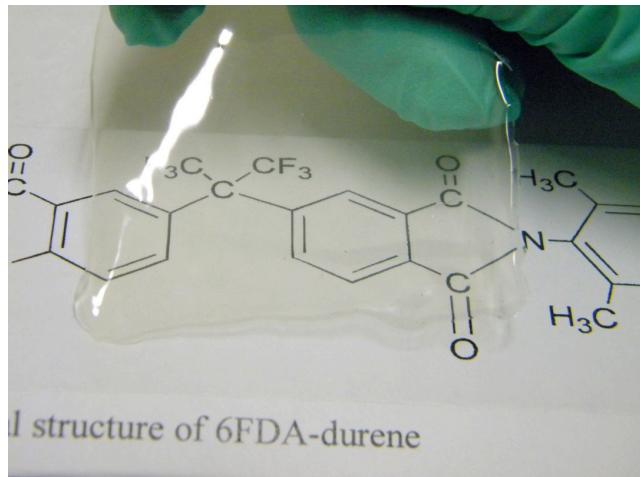
Cross-linked
6FDA-durene
 $\alpha \text{ H}_2/\text{CO}_2 = 100$



6FDA-durene

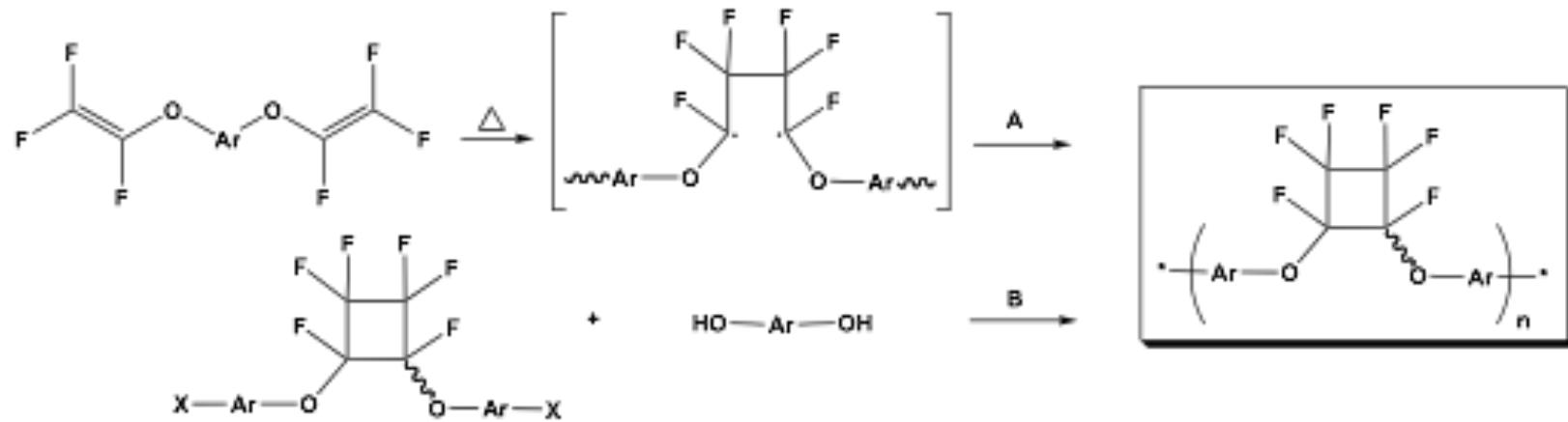
Yield 89%
Mw 54,000
PDI 1.79

6FDA-durene



Perfluorocyclobutyl (PFCB) polymers

- Excellent solution and melt processability
- High thermal/oxidative stability, chemical resistance
- $T_g = 150 - 300 \text{ }^\circ\text{C}$
- Easy, condensate-free polymerization

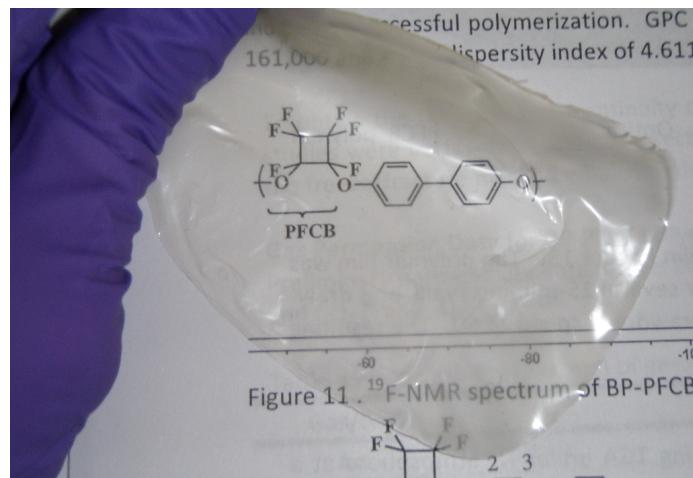


(A) Step-growth thermal [2+2] cyclodimerization of bis(trifluorovinyloxyether) biphenyls

(B) Condensation of 1,2-bis(arylether)hexafluorocyclobutyl halide and bisphenol monomers

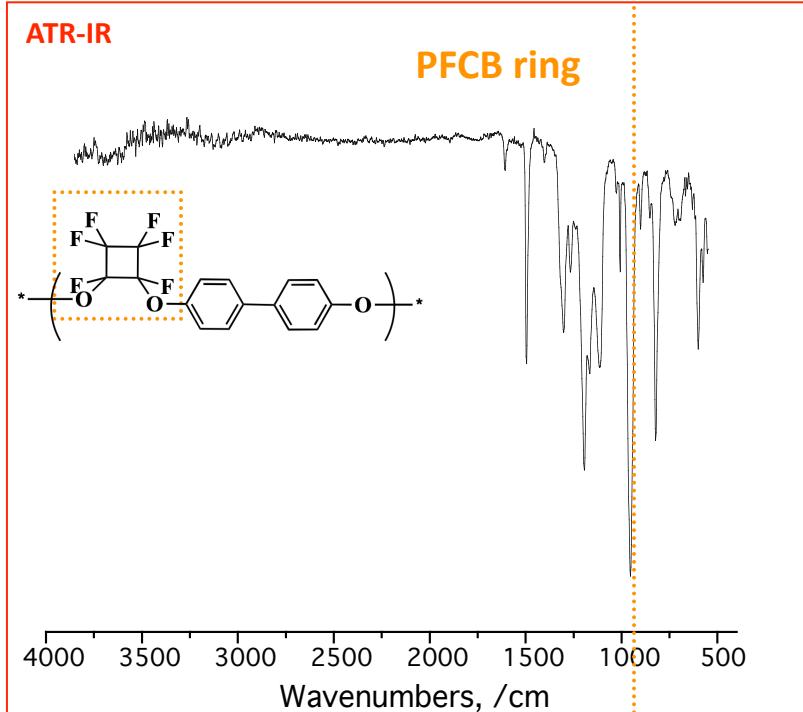
Smith Jr., D. W.; Chen, S.; Kumar, S.; Ballato, J.; Shah, H.; Topping, C.; Foulger, S. *Adv. Mater.* 2002, 14, 1585-1589.; Smith Jr., D. W.; Babb, D. A.; Shah, H. V.; Hoeglund, A.; Traiphob, R.; Perahia, D.; Boone, H. W.; Langhoff, C.; Radler, M. J. *Fluorine Chem.* 2000, 104, 109-117.; Kennedy, A. P.; Babb, D. A.; Bremmer, A. J.; Pasztor Jr., J.; *Polym. Sci.: Part A: Polym. Chem.* 1995, 33, 1859.

Optical image of biphenyl-PFCB polymer

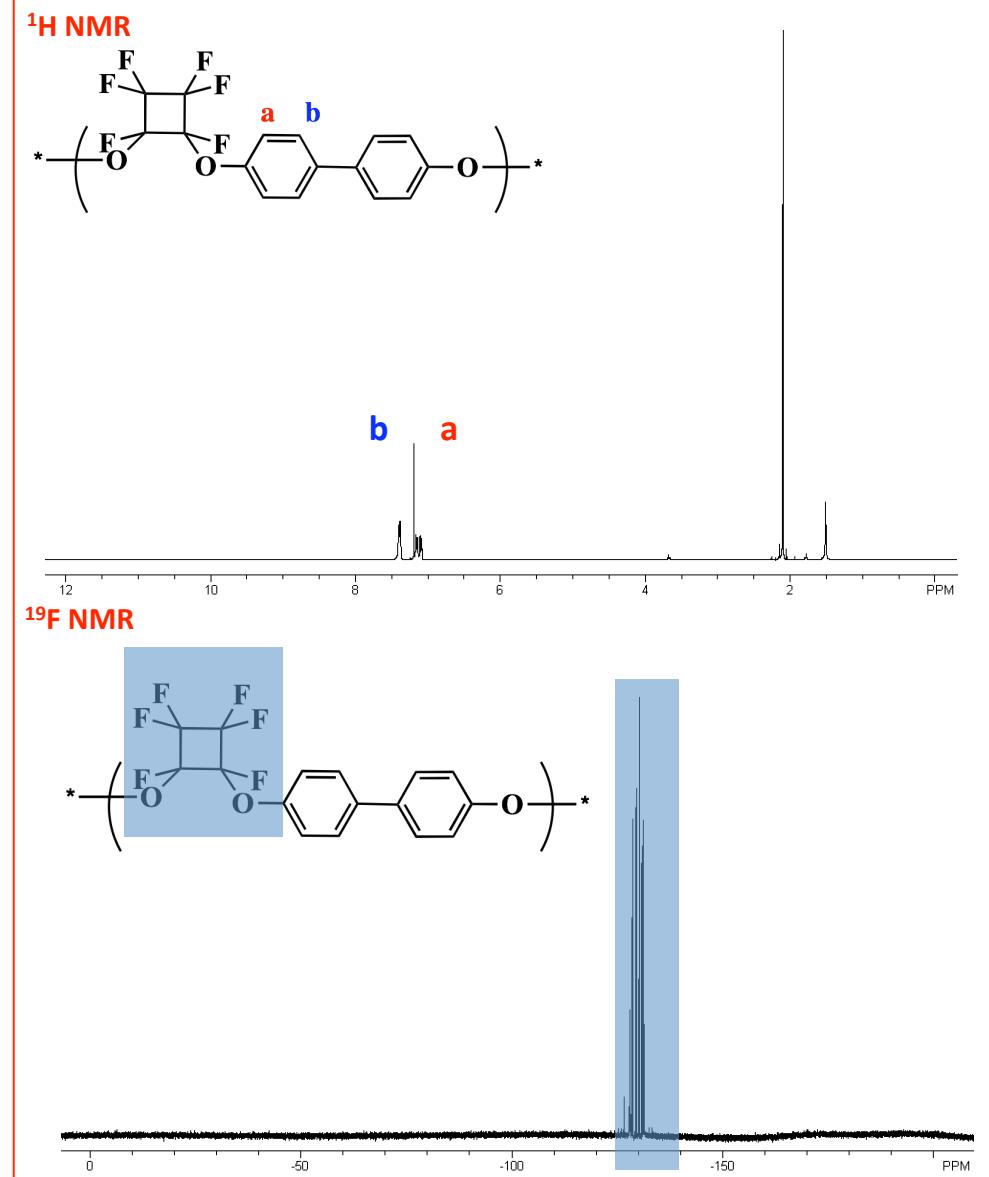


$M_w = 318,861$; PDI: 2.379

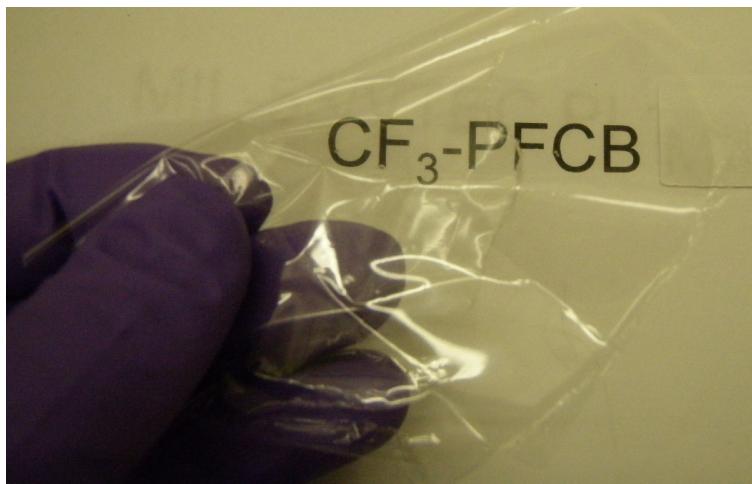
Thermal stability up to 440 °C



Biphenyl-PFCB Characterization

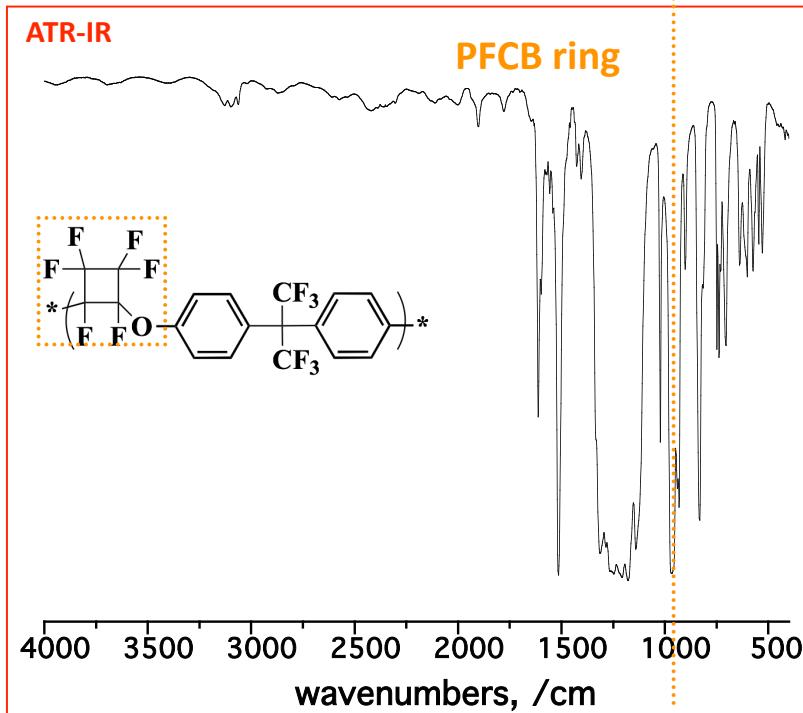


Optical image of $\text{CF}_3\text{-PFCB}$ polymer



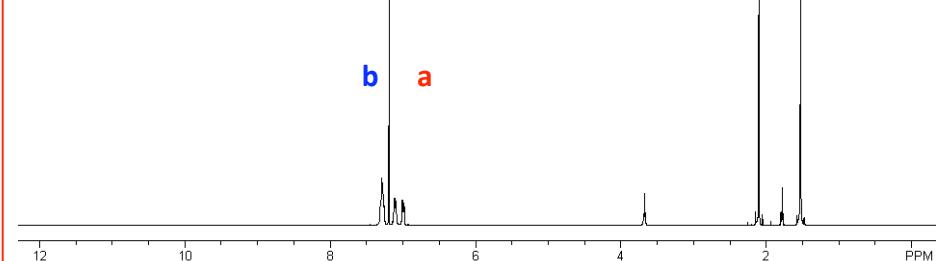
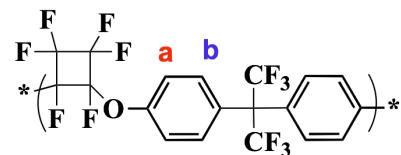
$M_w = 224,716$; PDI: 1.742

Thermal stability up to 450 °C

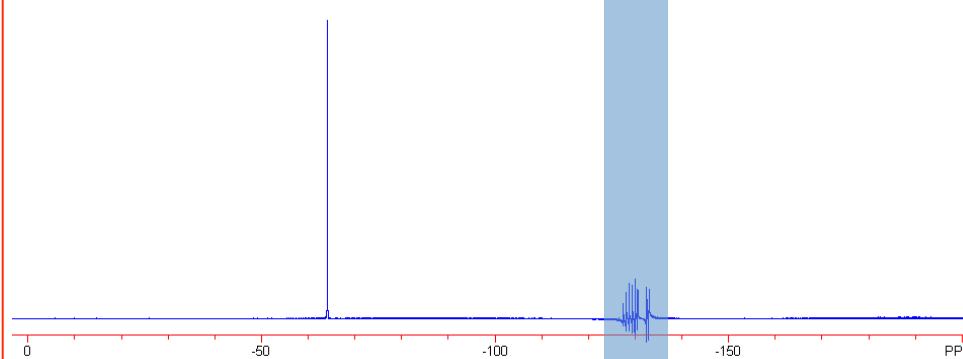
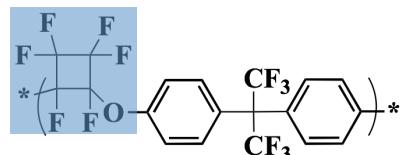


$\text{CF}_3\text{-PFCB}$ Characterization

¹H NMR

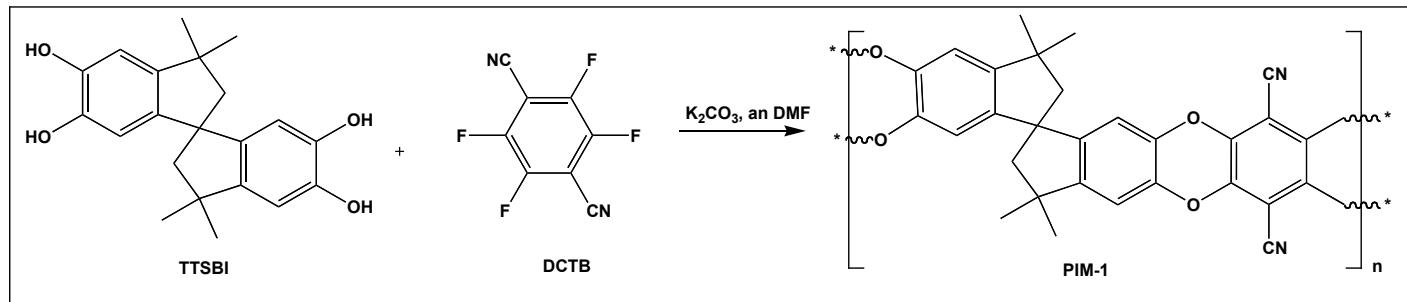


¹⁹F NMR

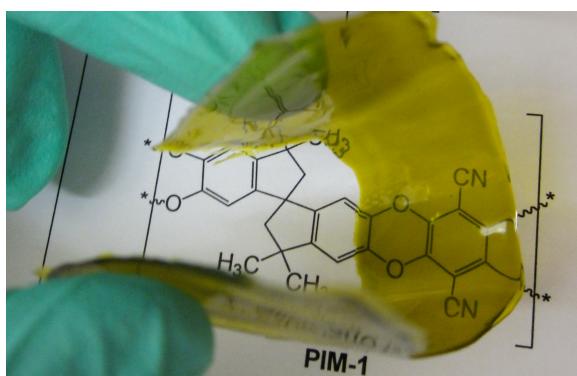


Polymers of Intrinsic Microporosity (PIM)

- Microporous materials containing interconnected pores (< 2 nm size) and large, accessible surface areas (300-1500 m²/g)
- Highly processable and easily fabricated into thin membranes
- Exhibit high gas permeability and good selectivity



Optical image of PIM-1 polymer



$M_w = 54,298^*$; PDI: 2.140

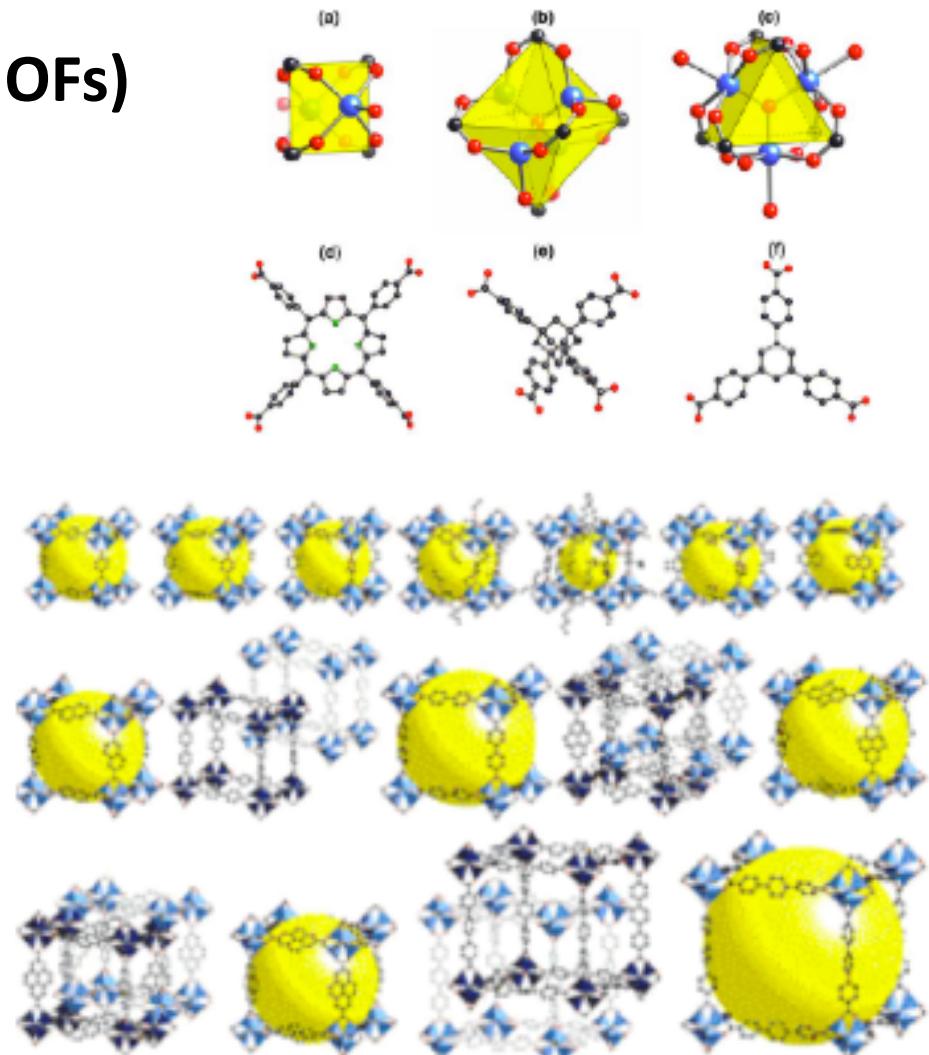
*Current work involves increasing M_w



Metal-Organic Frameworks and Zeolithic Imidazolate Frameworks

- **Metal-Organic Frameworks (MOFs)**

- Nanoporous materials
 - secondary building units
 - metal ion clusters
 - organic bridging ligands
 - strong chemical bonds
 - geometric structures
- Properties
 - high surface area
 - controlled porosity
 - functionalizable pore walls
 - affinity for gases
 - flexible chemical composition

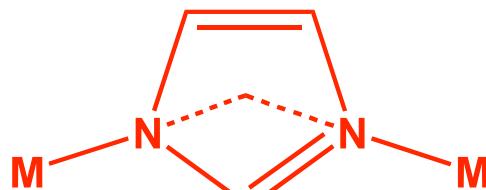


Zeolithic Imidazolate Frameworks

ZIFs employ imidazolate ligands to bind to tetrahedral divalent metal ions

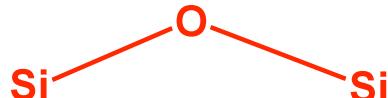
Isostructural with several zeolite analogs, similar bond angles

Microporous – potentially enhancing gas selectivity



Similar bond angles

K. Park et al *PNAS* 103 (2006) 10186

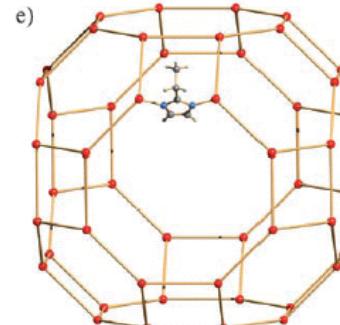
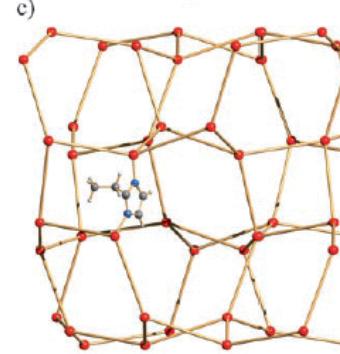
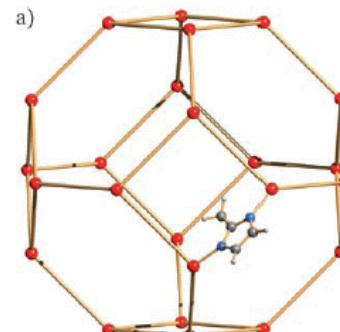


SOD

Zeolite analogs

ANA

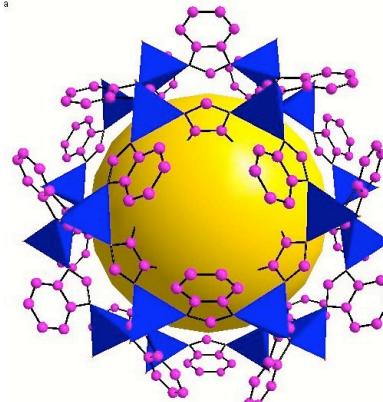
RHO



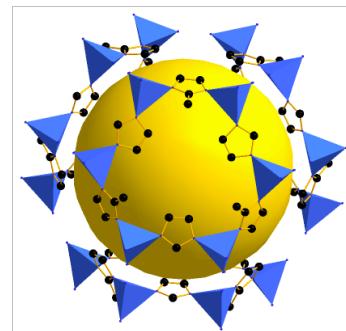
Huang et al *Angew. Chem. Int. Ed.* 45 (2006) 1557

Targeted ZIFs for H₂ Separations

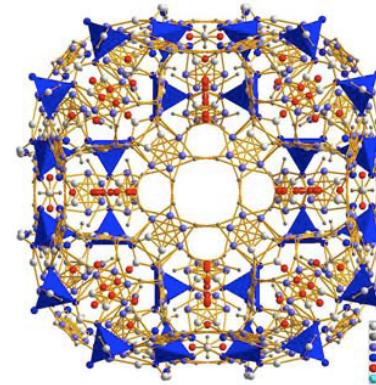
ZIF	Pore Size (nm)	Pore Aperture (nm)	Sieving
ZIF-7	0.9 – 1.1	0.30	H ₂
ZIF-8	1.1	0.34	H ₂
ZIF -20	1.4	0.45	H ₂ , CO ₂
ZIF-69	0.72	0.44	H ₂ , CO ₂
ZIF-90 and derivatives	1.12	0.35	H ₂
ZIF-95	2.4	0.36	H ₂
ZIF-100	3.6	0.33	H ₂
MIL-53	n/a	0.8	H ₂



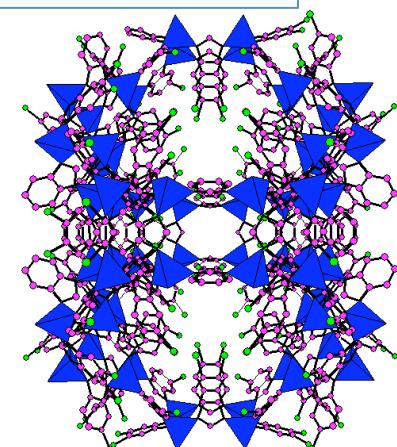
ZIF-7



ZIF-8



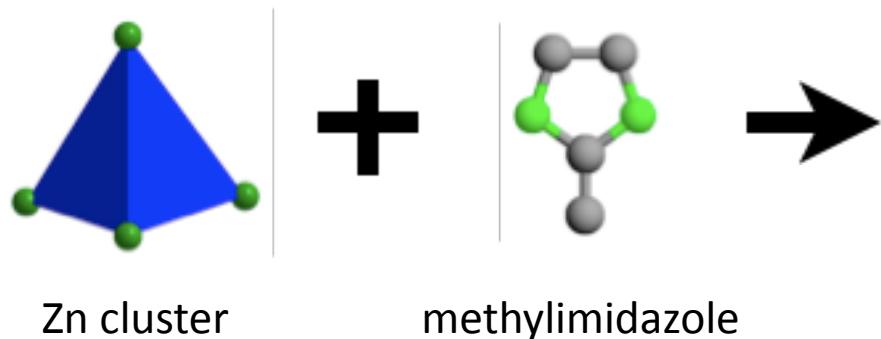
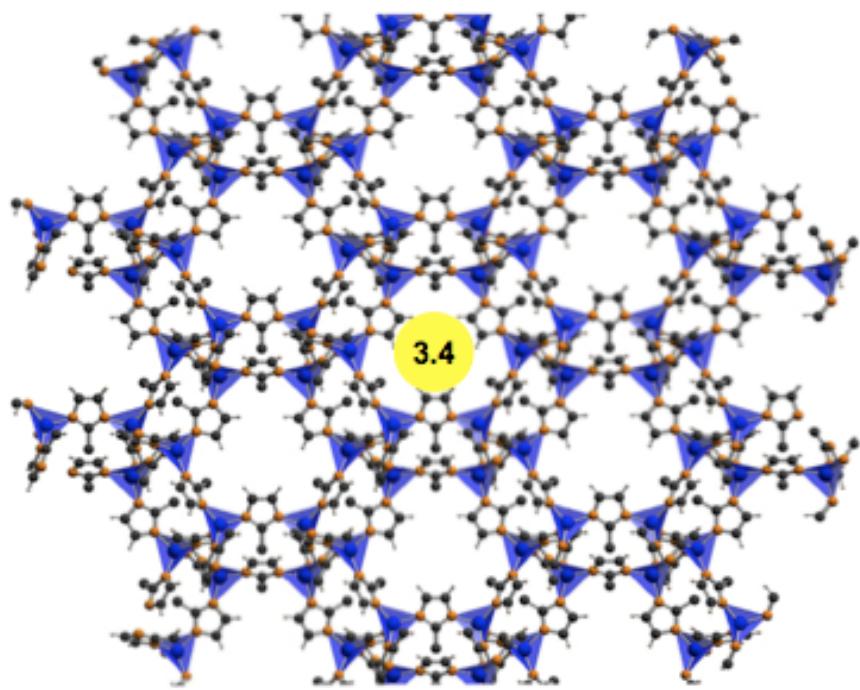
ZIF-20



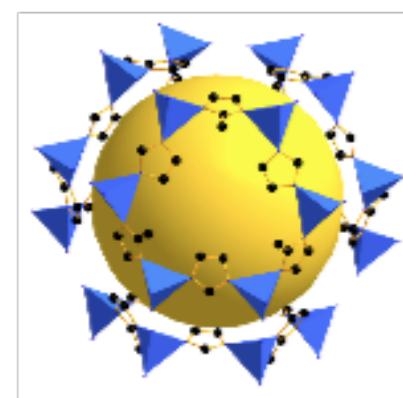
ZIF-95



Selected ZIF MMMs

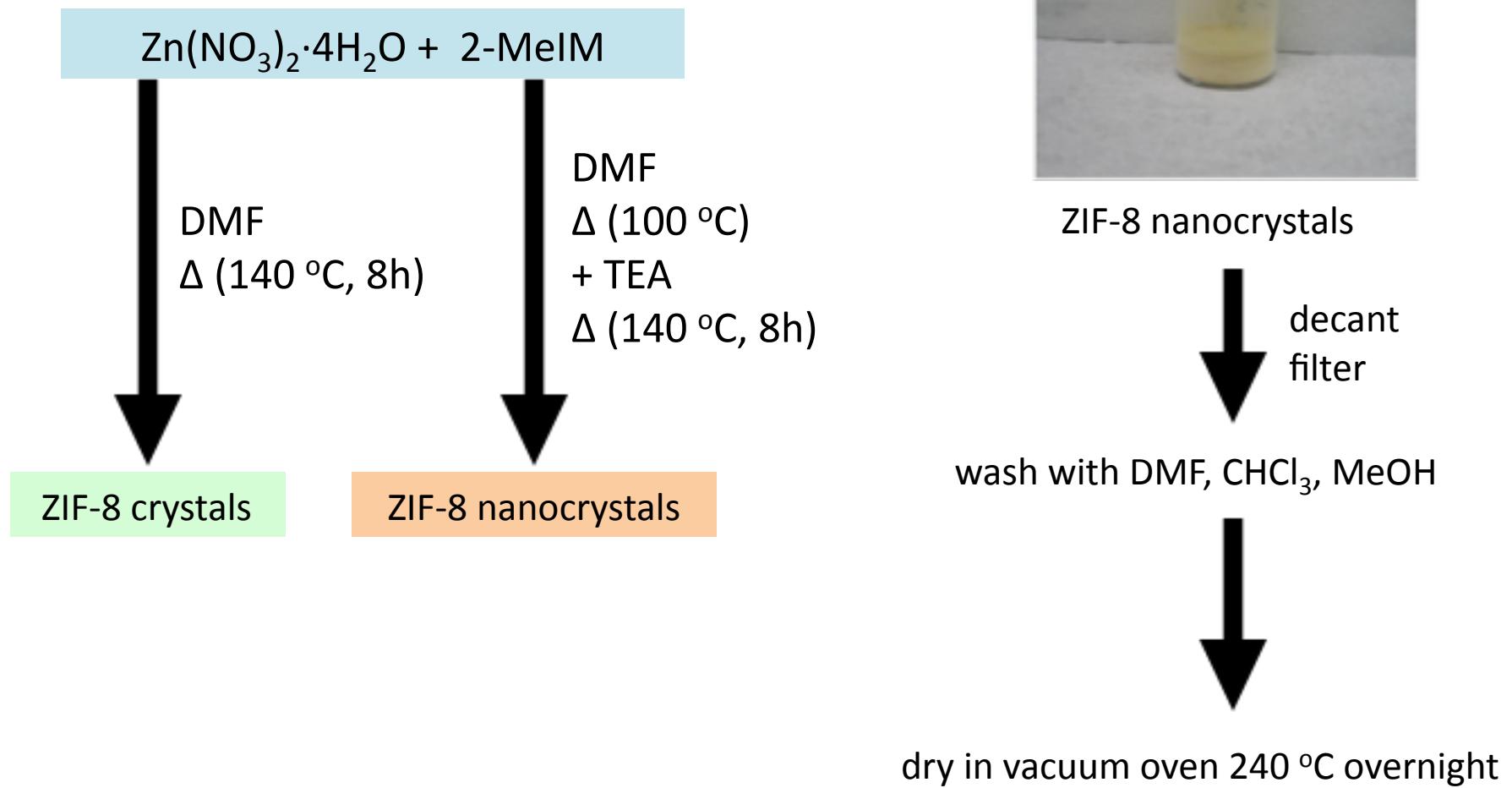


- zeolite-type MOF
- zinc metal clusters and 2-methylimidazole ligands
- sodalite structure
- surface area: $>1600 \text{ m}^2/\text{g}$
- cage size: 11.6 \AA
- pore aperture: 3.4 \AA
- **Stable to steam and H_2S at 250°C**



ZIF-8

Synthesis Scheme

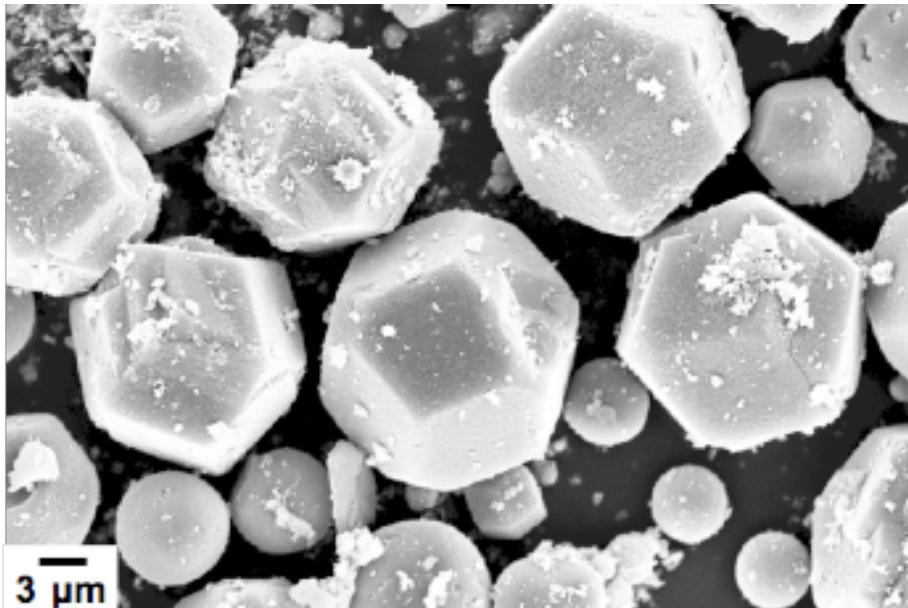


Park, K.S.; Ni, Z.; Cote, A.; PNAS, 2006, 103, 10186-10191

Huang, L.; Wang, H.; Chen, J.; et al., Microporous Mesoporous Mater, 2003, 58, 105-114

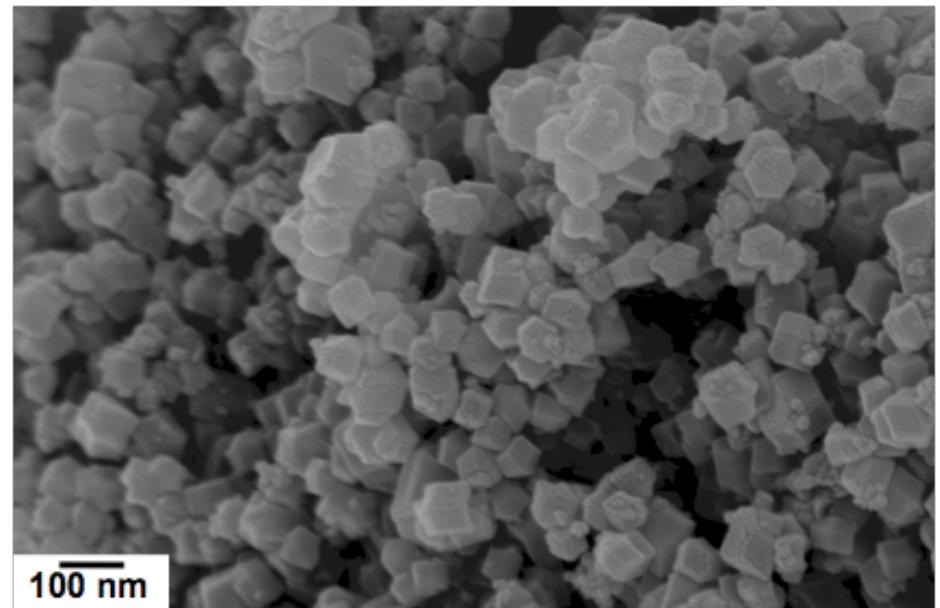
Scanning Electron Microscopy (SEM)

ZIF-8 without TEA



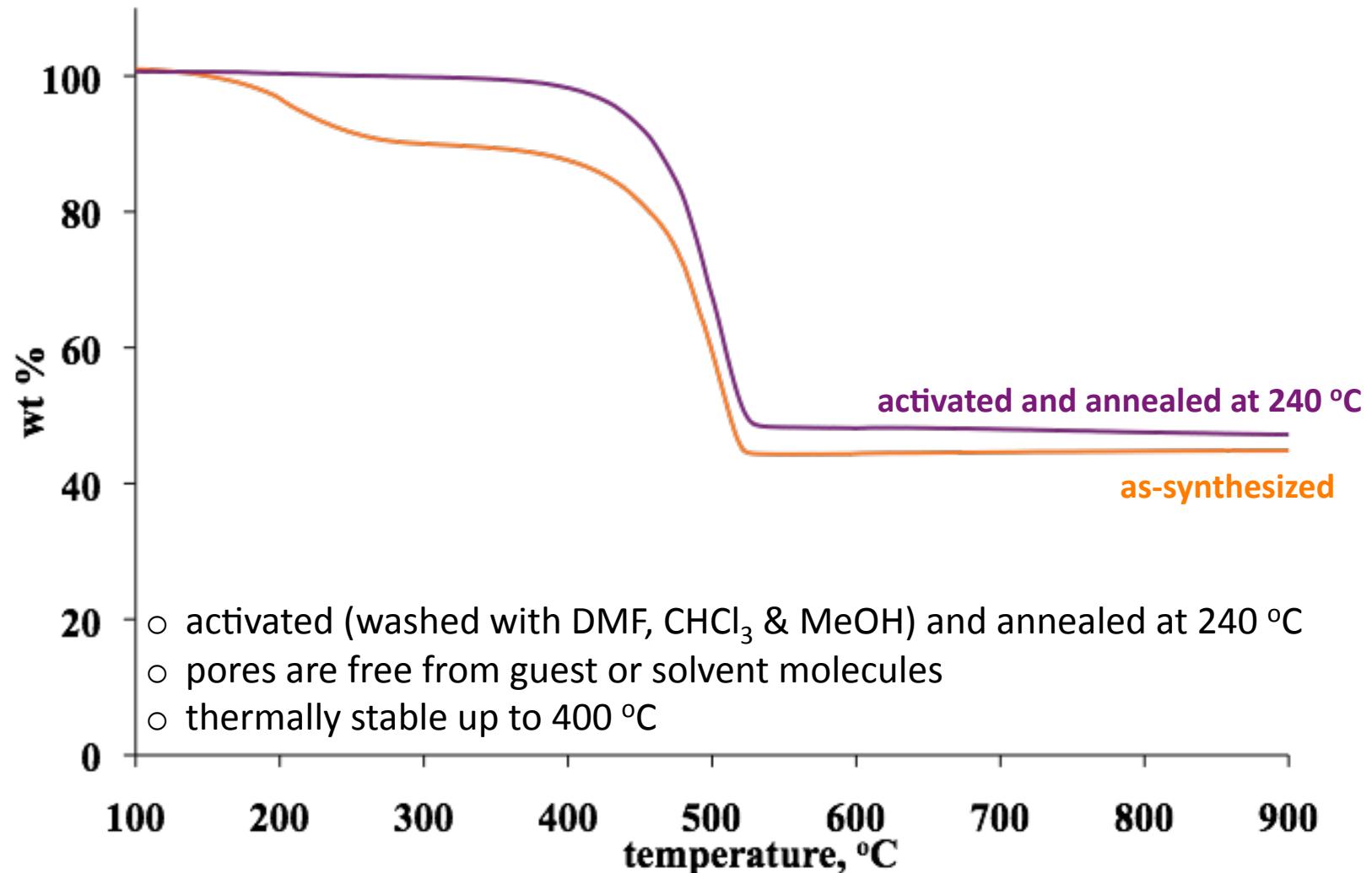
microcrystals

ZIF-8 with TEA

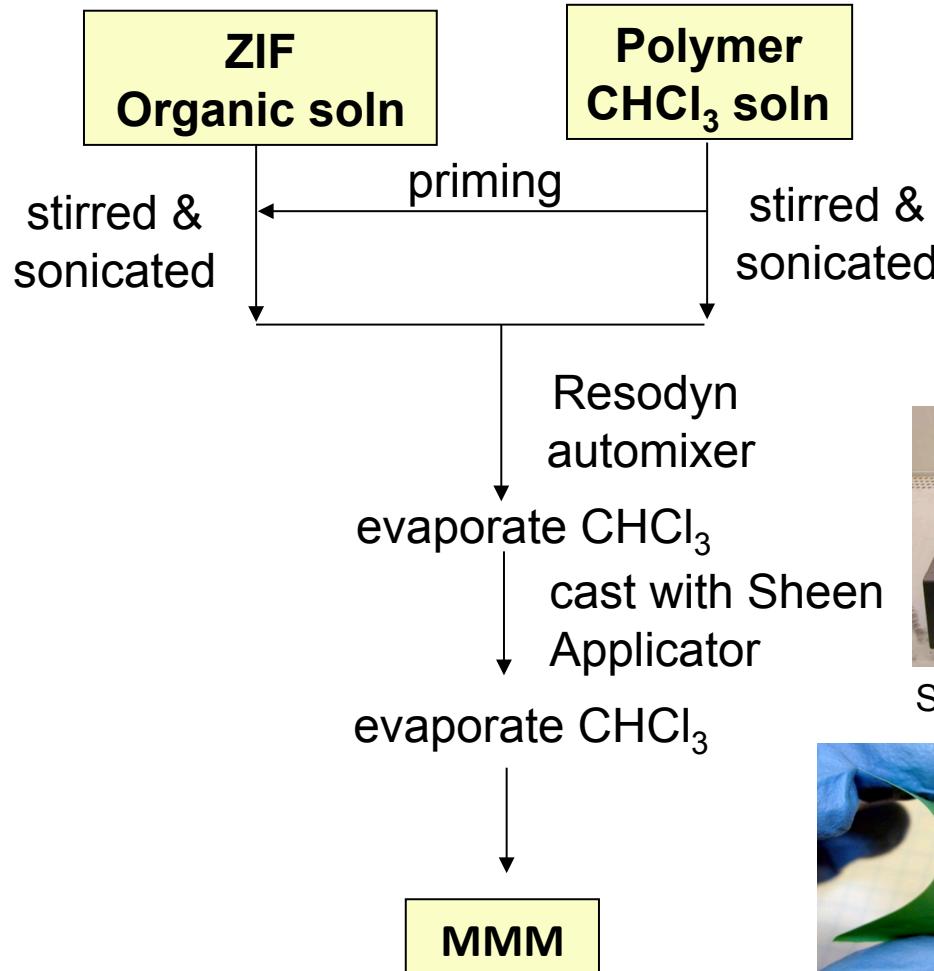


nanocrystals

Thermogravimetric Analysis of ZIF-8



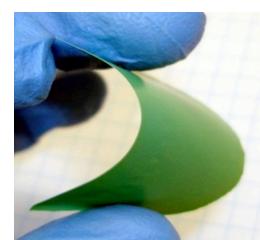
MMM Fabrication



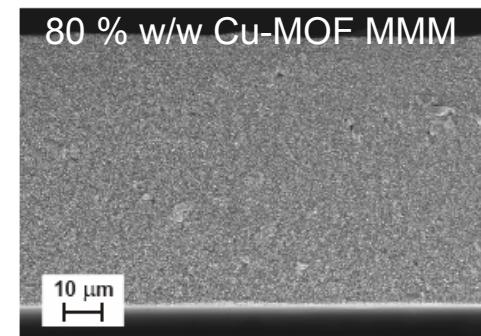
LabRAM Mixer
Resodyn Acoustic Mixer



Sheen Automatic Applicator



MMM

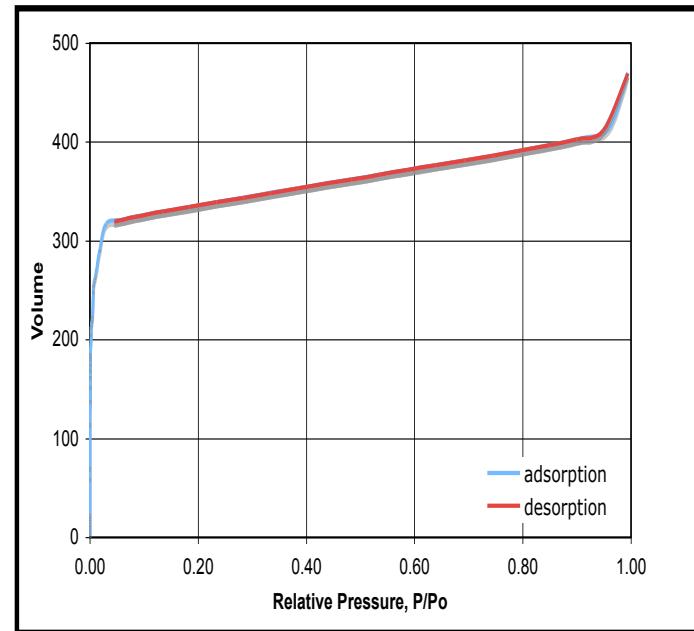


SEM image of MMM cross-section

Characterization Methods

- X-ray diffraction
- Scanning electron microscopy
- Transmission electron microscopy
- Atomic force microscopy
- FTIR
- Raman spectroscopy
- Mechanical testing
- Thermogravimetric analysis
- GPC
- DSC
- N₂/Ar adsorption

- N₂ adsorption analysis



ZIF-8 N₂ adsorption isotherm

BET surface area = 1200 m²/g

Porosity = 6.2 Å

High Pressure Volumetric Analyzer

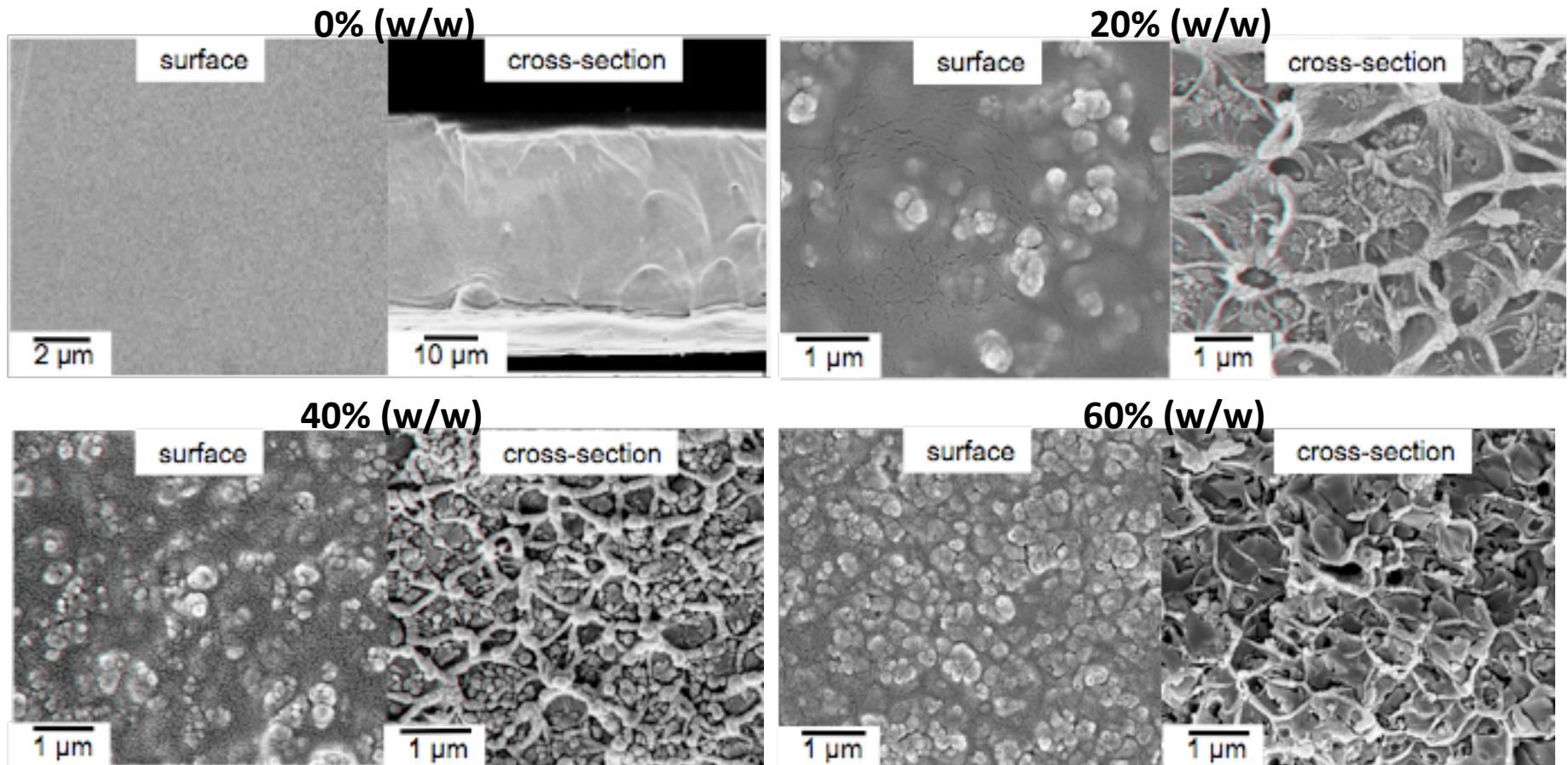


HPVA-100

Features

- N₂, H₂, CH₄, Ar, O₂, CO and CO₂
- Operating pressure from mtorr to 200 atm
- Operating temperature from cryogenic to 500 °C
- Used to measure gas solubility in polymers and porous materials

$$P = D \times S$$

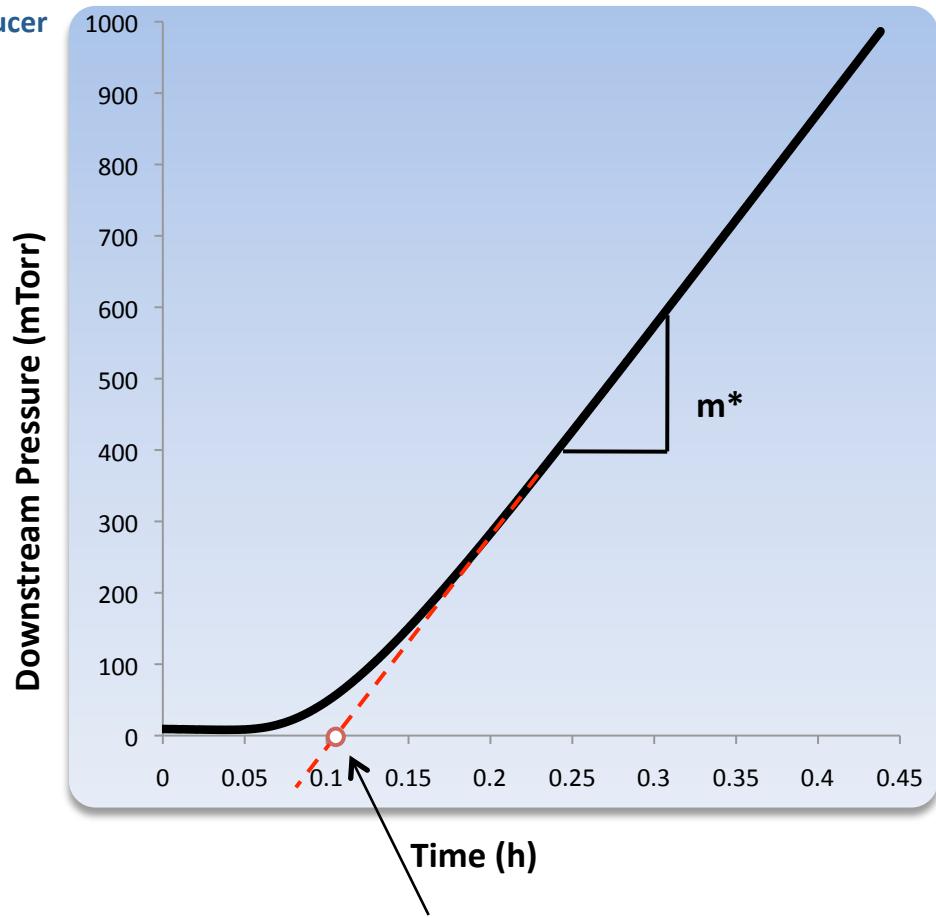
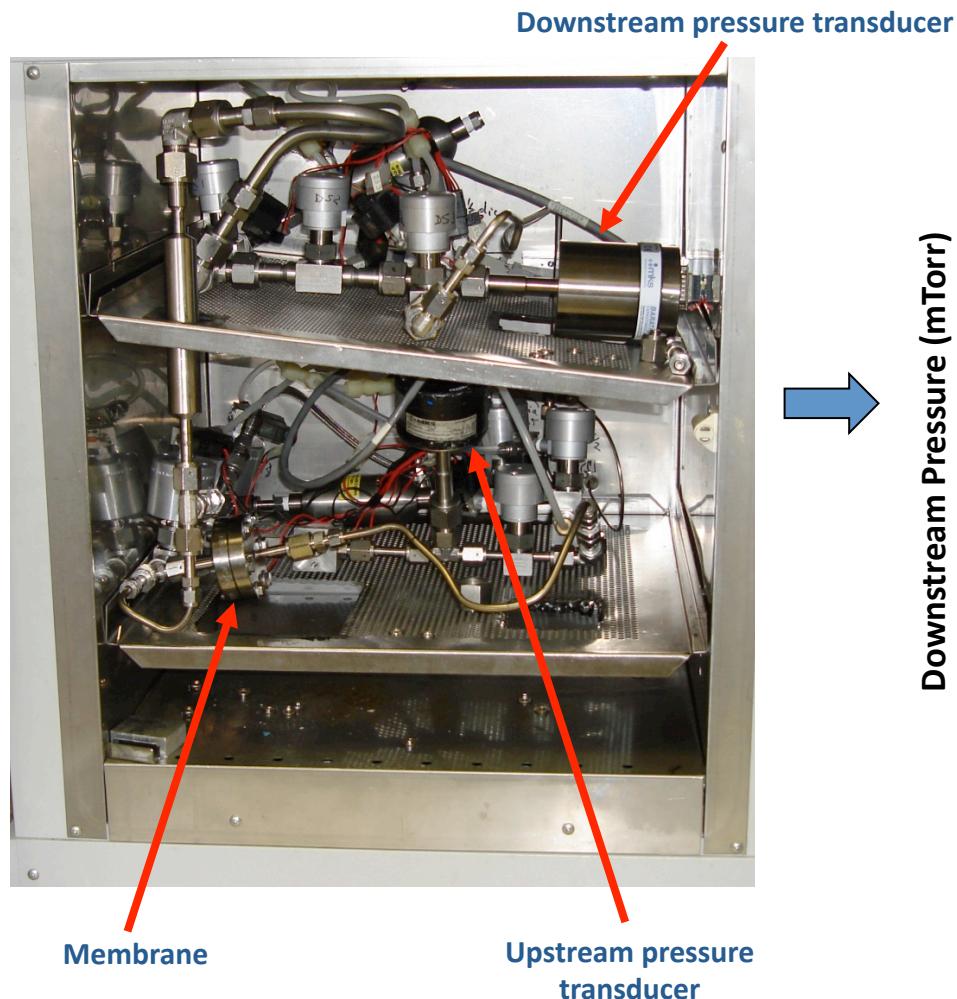


- increase in particle content with increase in loading
- good dispersion of ZIF-8 material in the polymer matrix
- membrane thickness is 40-50 μm

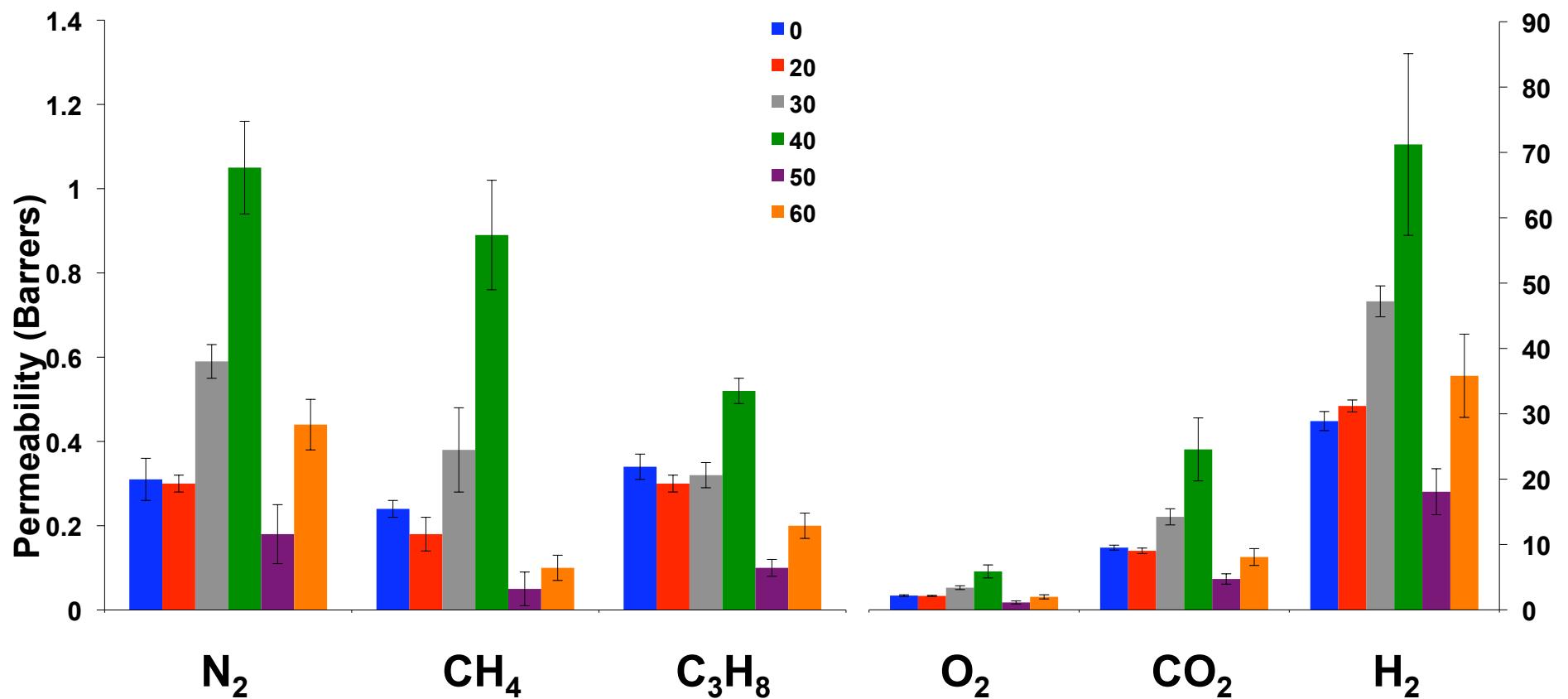
Membrane Permeability Tests

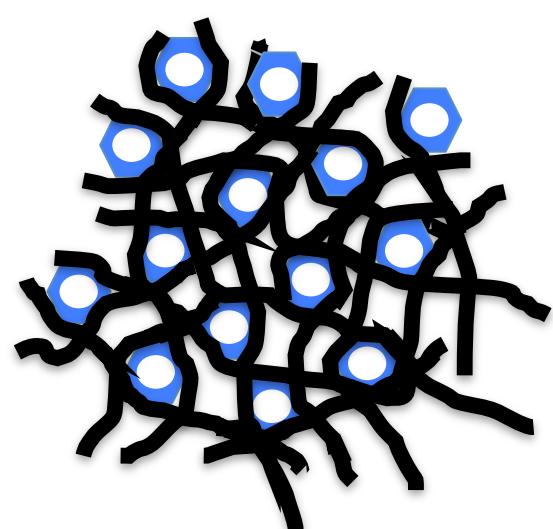
Two custom-built permeameters operating at 3 atm and 35 °C

Pure gases: H₂, O₂, N₂, CH₄, CO₂, C₃H₆, C₃H₈
Gas mixtures: H₂/CO₂, CO₂/CH₄, CH₄/N₂, C₃H₆/C₃H₈

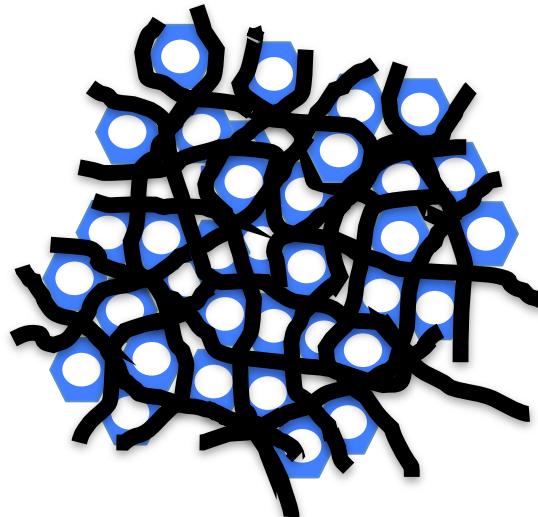


Time lag (θ): time required for the gas to go through the membrane (used to calculate diffusivity)

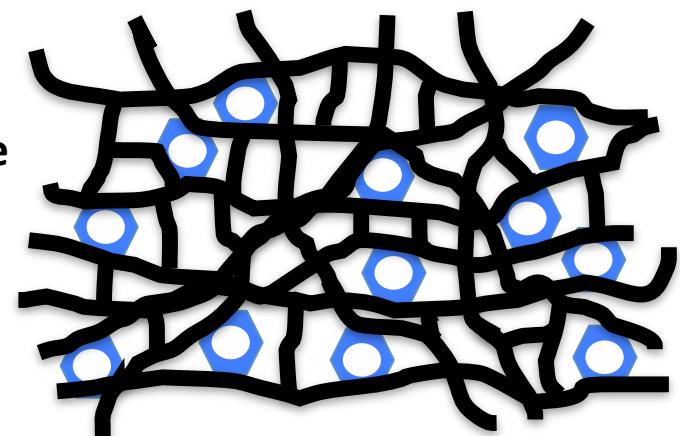




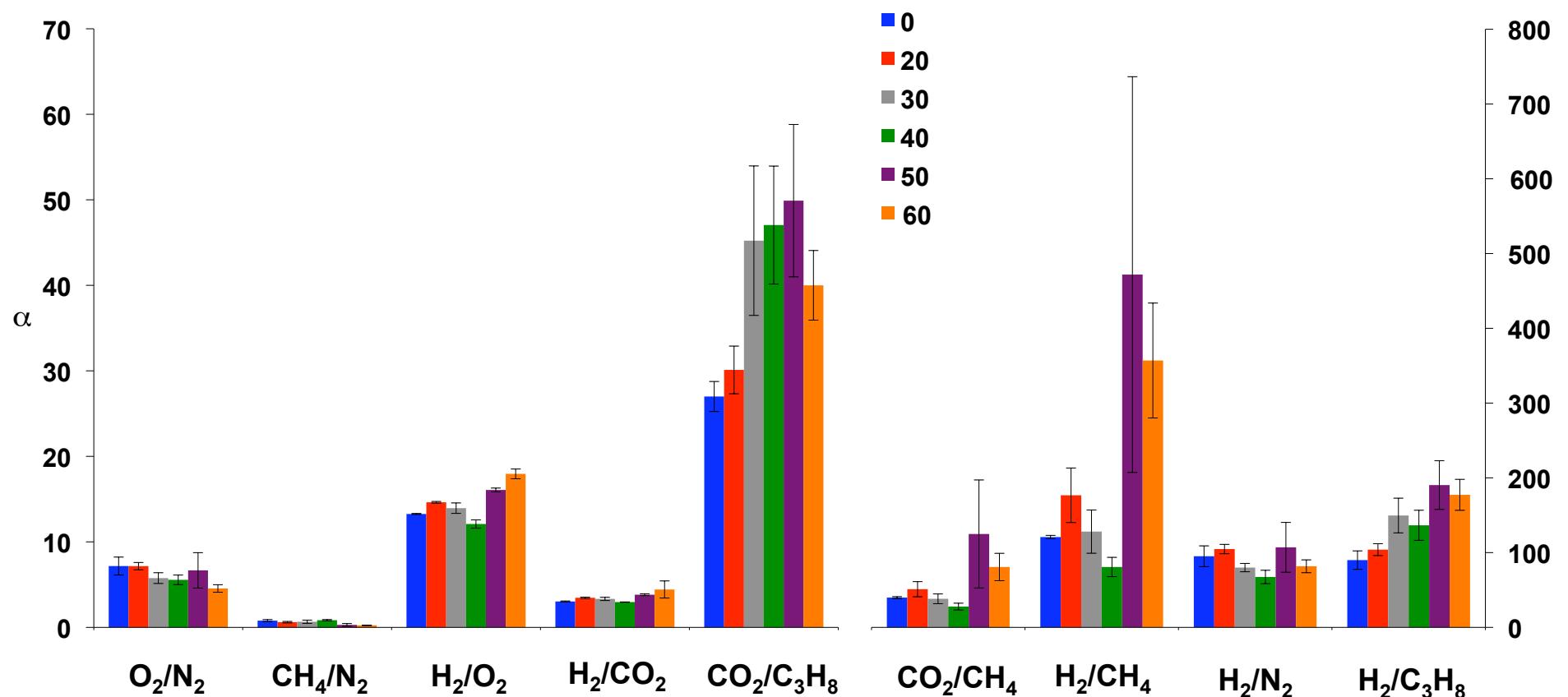
nanoparticles create
more polymer free volume, $P \uparrow$



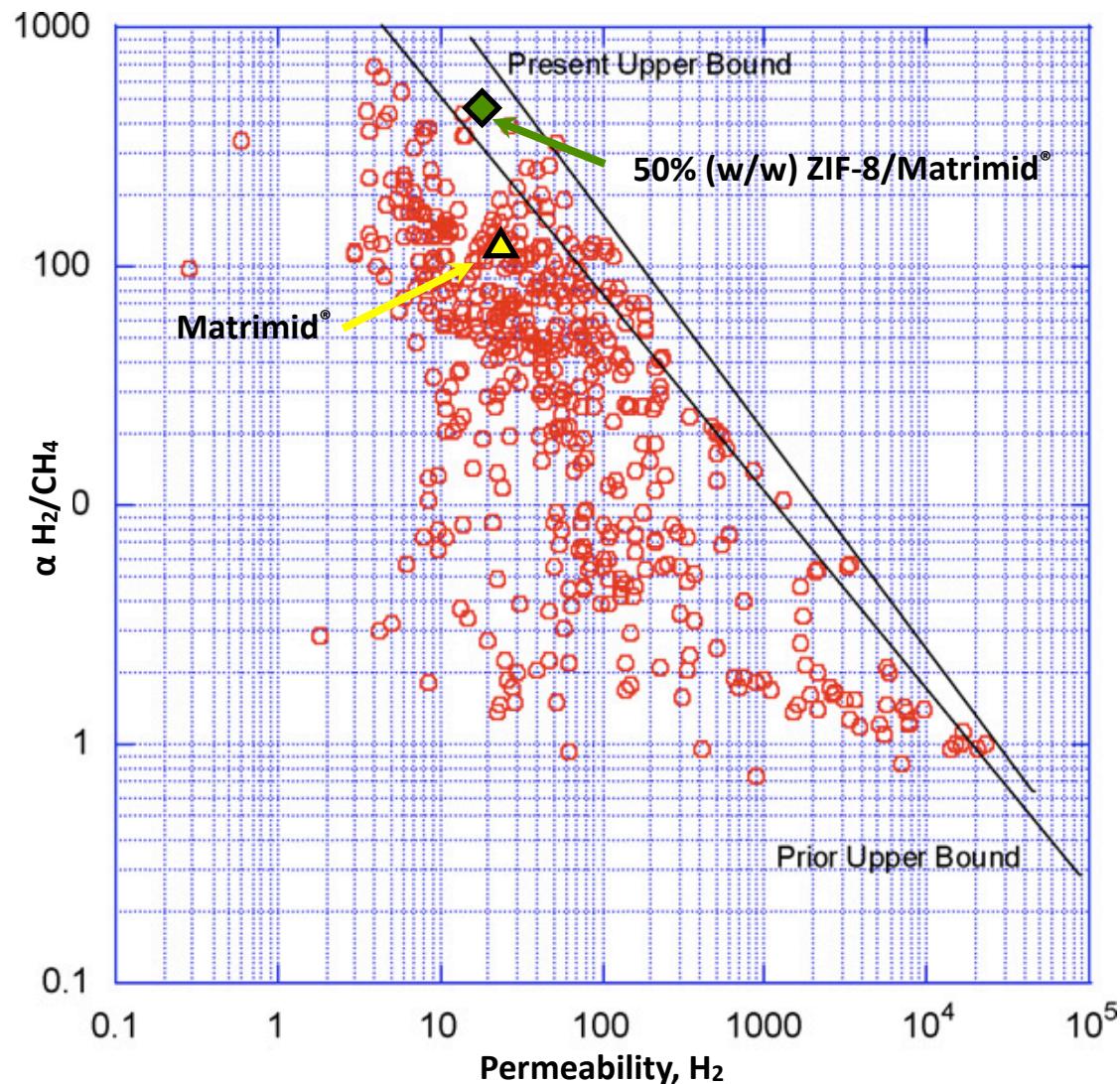
At high loadings
penetrants forced
to go through
nanoparticle pores,
 P depends on pore size



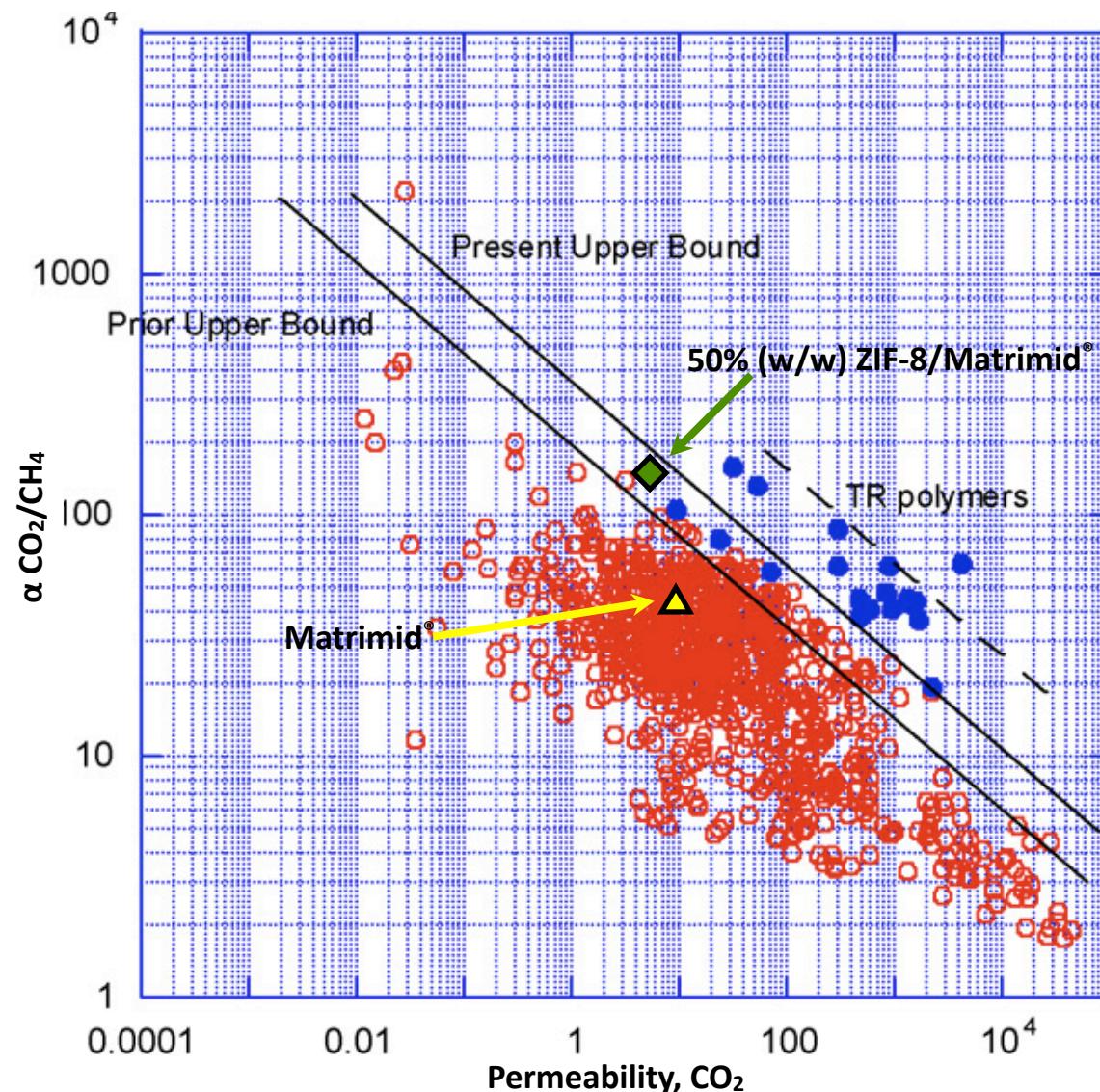
cross-linked/rigidified
polymer matrix, $P \downarrow$



Robeson Plot



Robeson Plot

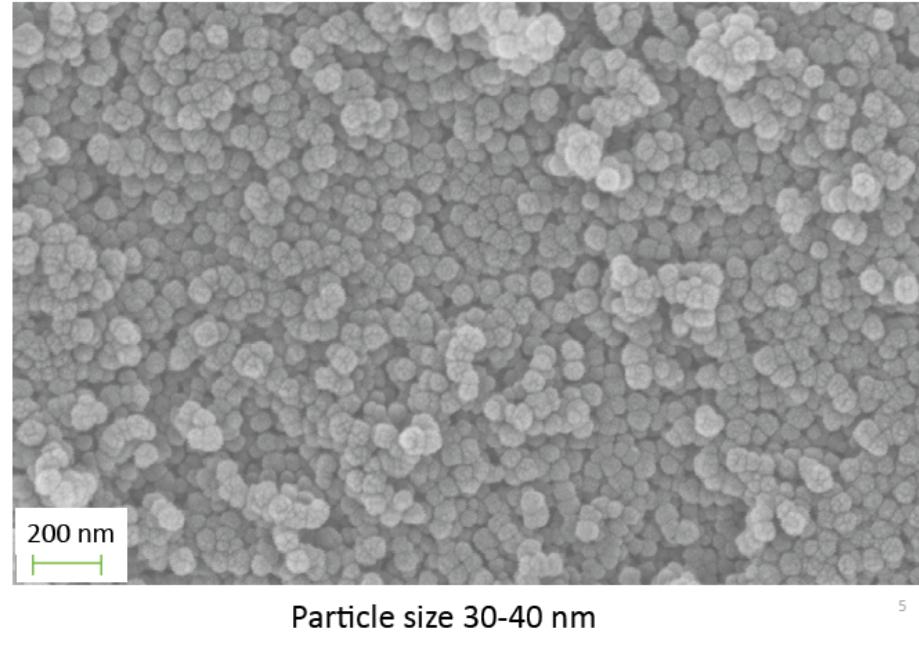


- Zeolite-type MOF
- Zinc metal clusters and benzimidazole ligands
- Sodalite structure
- Cage size: 0.9 - 1.1 nm
- Pore aperture: 3.0 Å

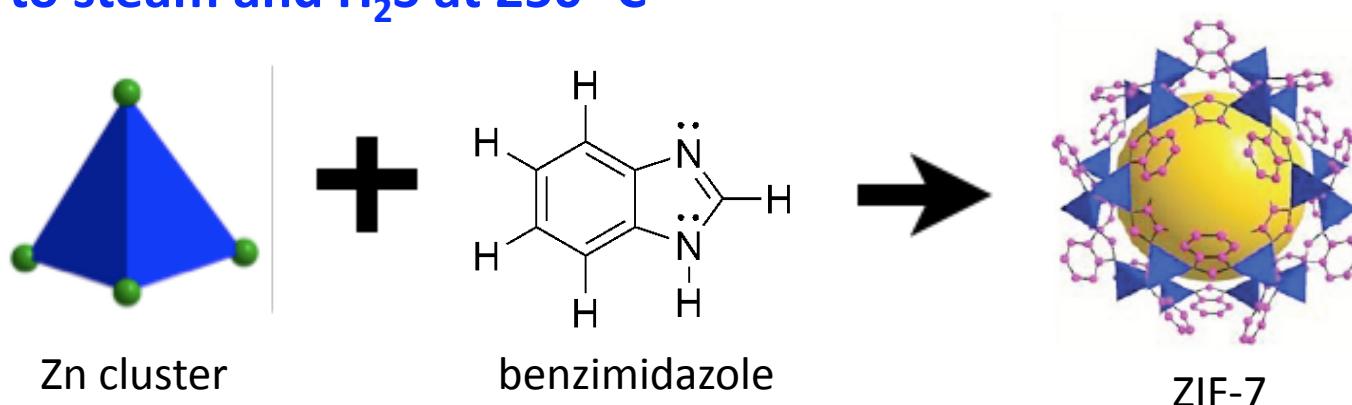
Kinetic diameter H_2 = 2.89 Å

CO_2 = 3.3 Å

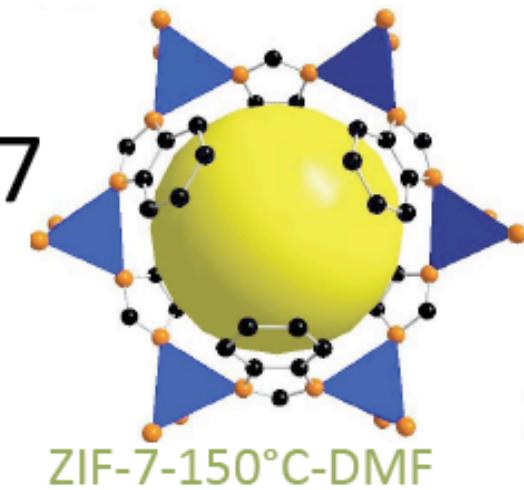
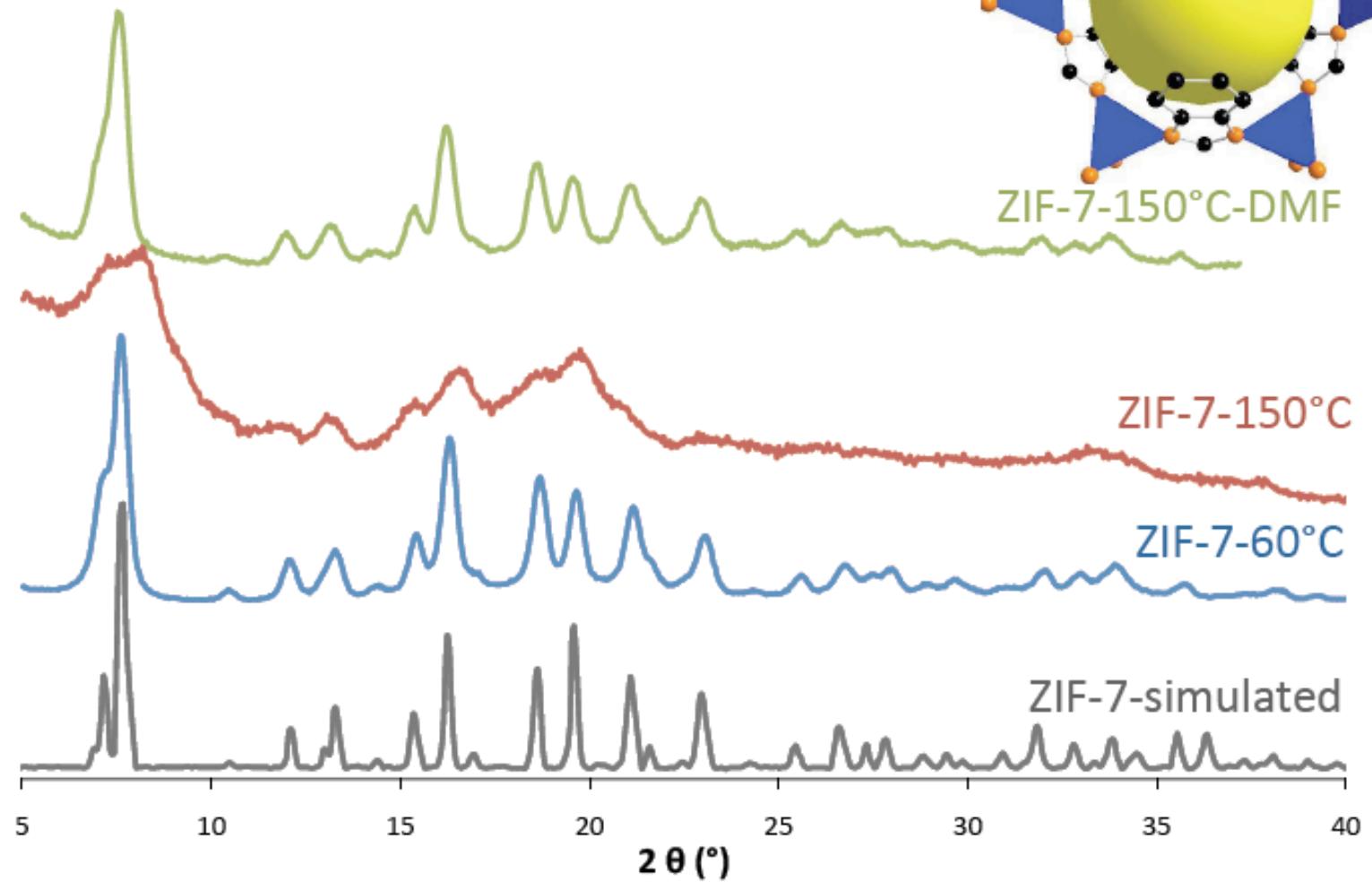
- **Stable to steam and H_2S at 250 °C**



5



XRD plot of ZIF-7

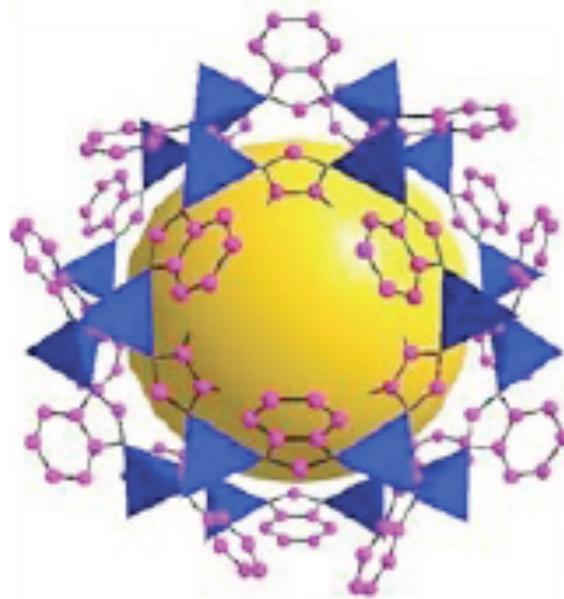


ZIF-7-150°C-DMF

ZIF-7-150°C

ZIF-7-60°C

ZIF-7-simulated



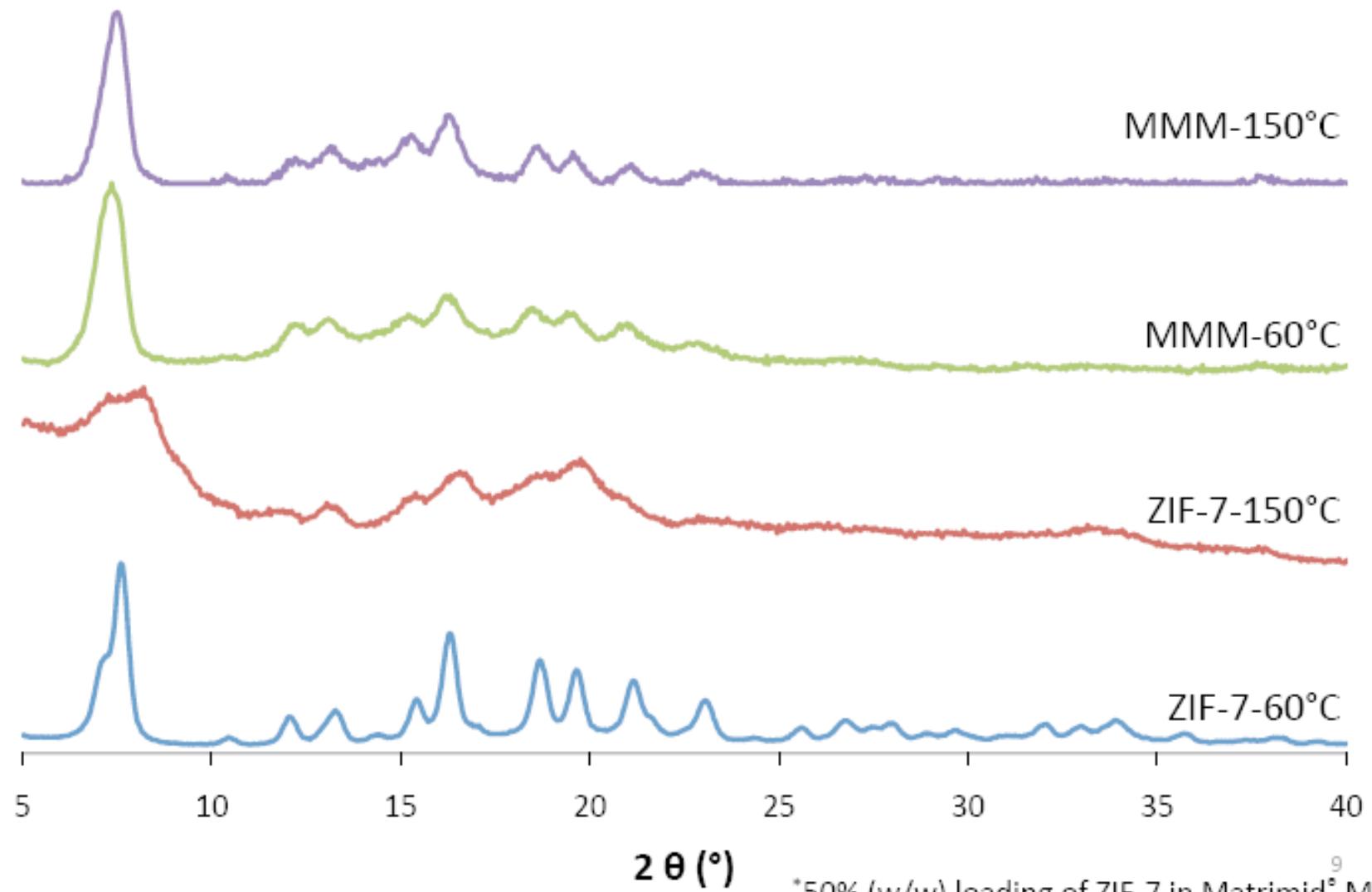
ZIF-7

**50% ZIF-7/Matrimid®
mixed-matrix membrane**

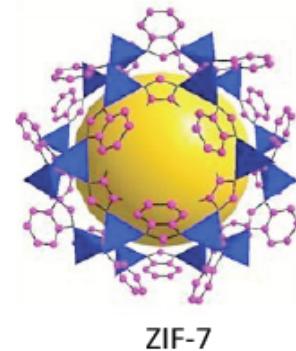
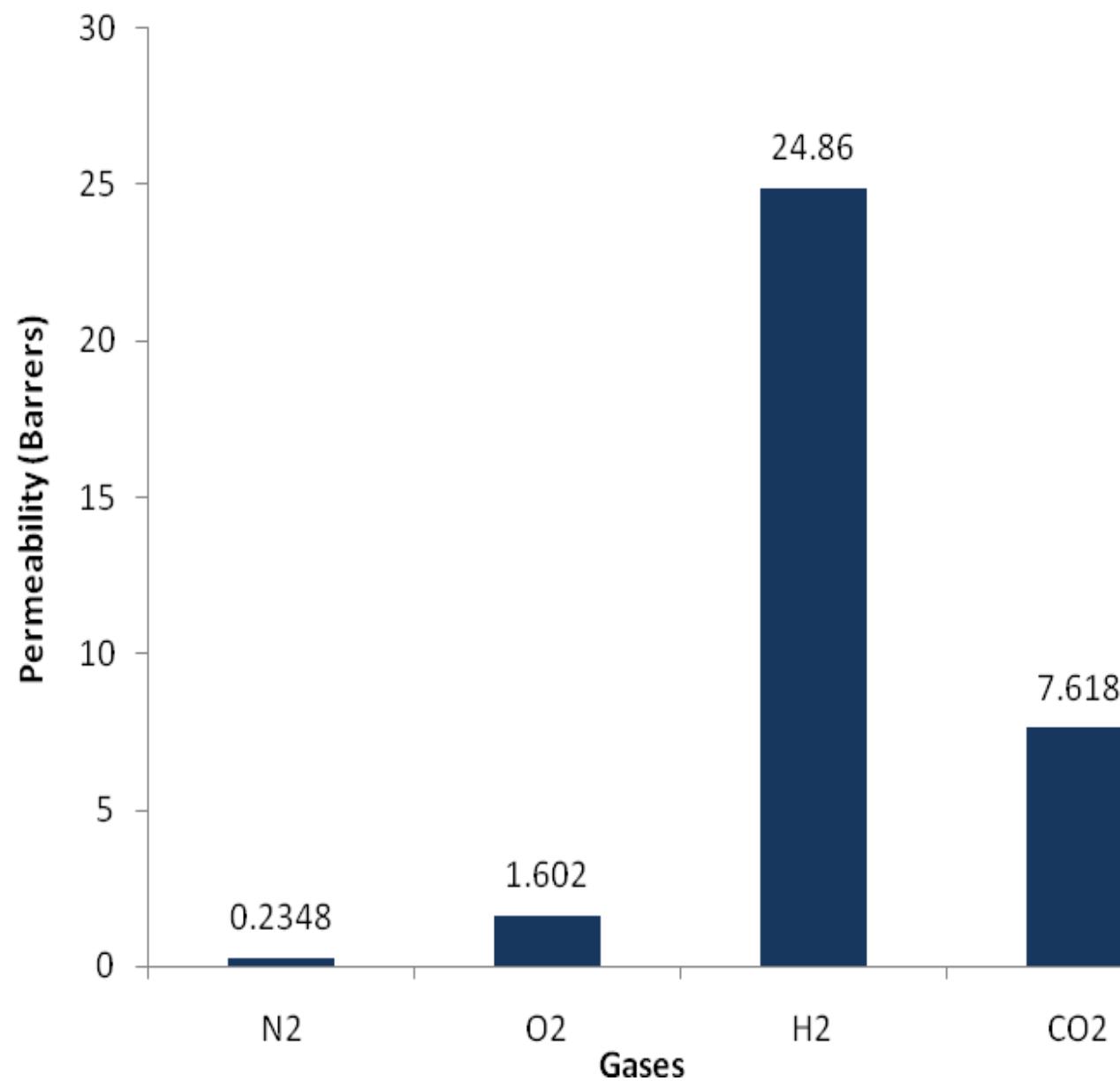
70% (w/w) ZIF-7/Matrimid® MMM

**Highly
transparent and
flexible films**

XRD of ZIF-7 and MMMs*



*50% (w/w) loading of ZIF-7 in Matrimid® MMM



Ideal selectivity ($\alpha_{A/B}$)	50% (w/w) ZIF-7/ Matrimid® MMM
H ₂ /CO ₂	3.26
O ₂ /N ₂	6.88
H ₂ /O ₂	15.52
H ₂ /N ₂	106.7

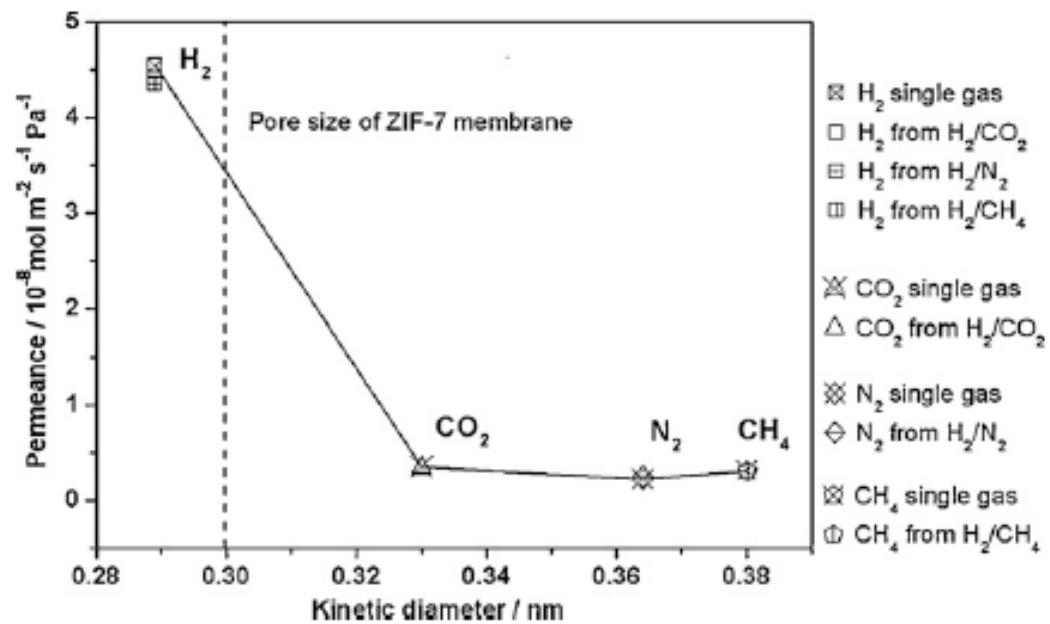
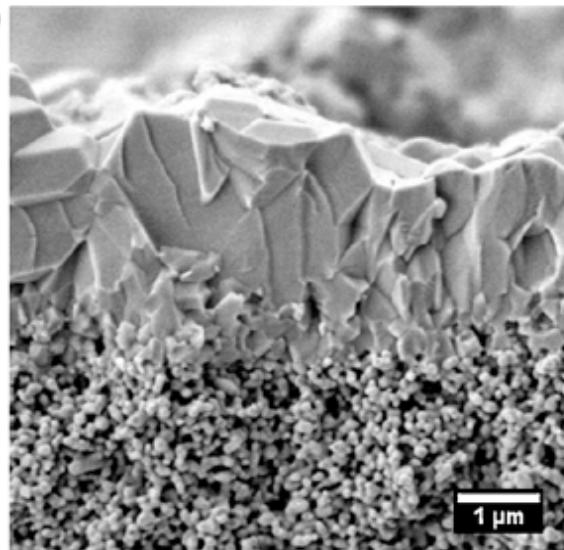
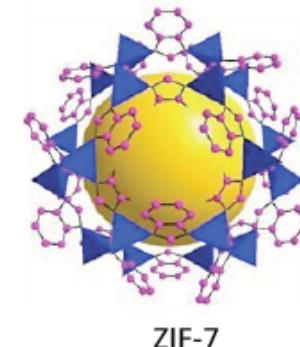
$$\alpha_{A/B} = P_A / P_B$$

Kinetic diameter

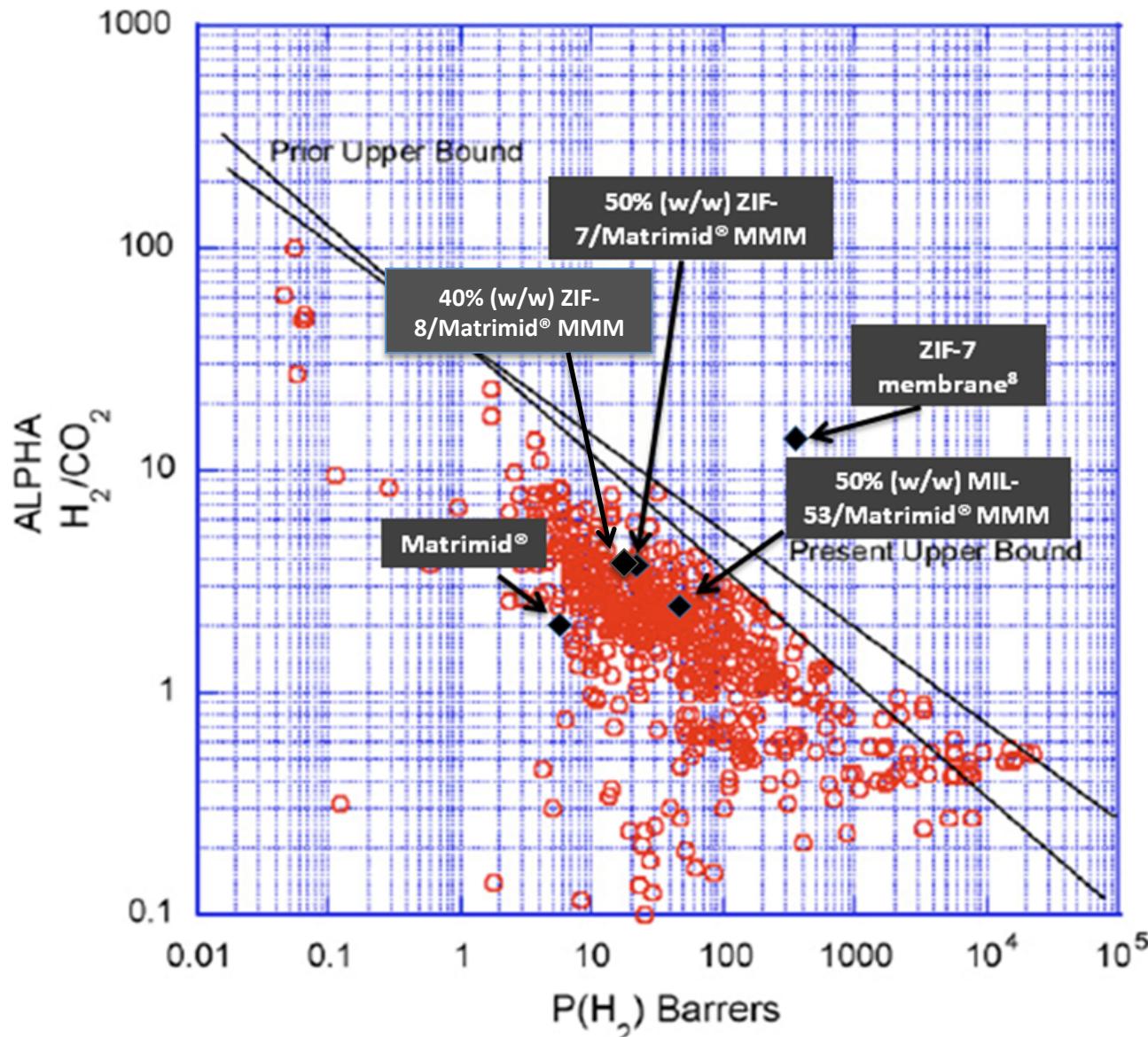


ZIF-7 membrane

$H_2/CO_2 = 13$ at $220^\circ C$



Robeson Plot



Compared to Matrimid®, 50% (w/w) ZIF-7 has 4x increase in permeability and 2x increase in selectivity.



High Temperature-High Pressure Permeameter

Membranes

HPHT Permeameter Design

Diagram showing components of apparatus:

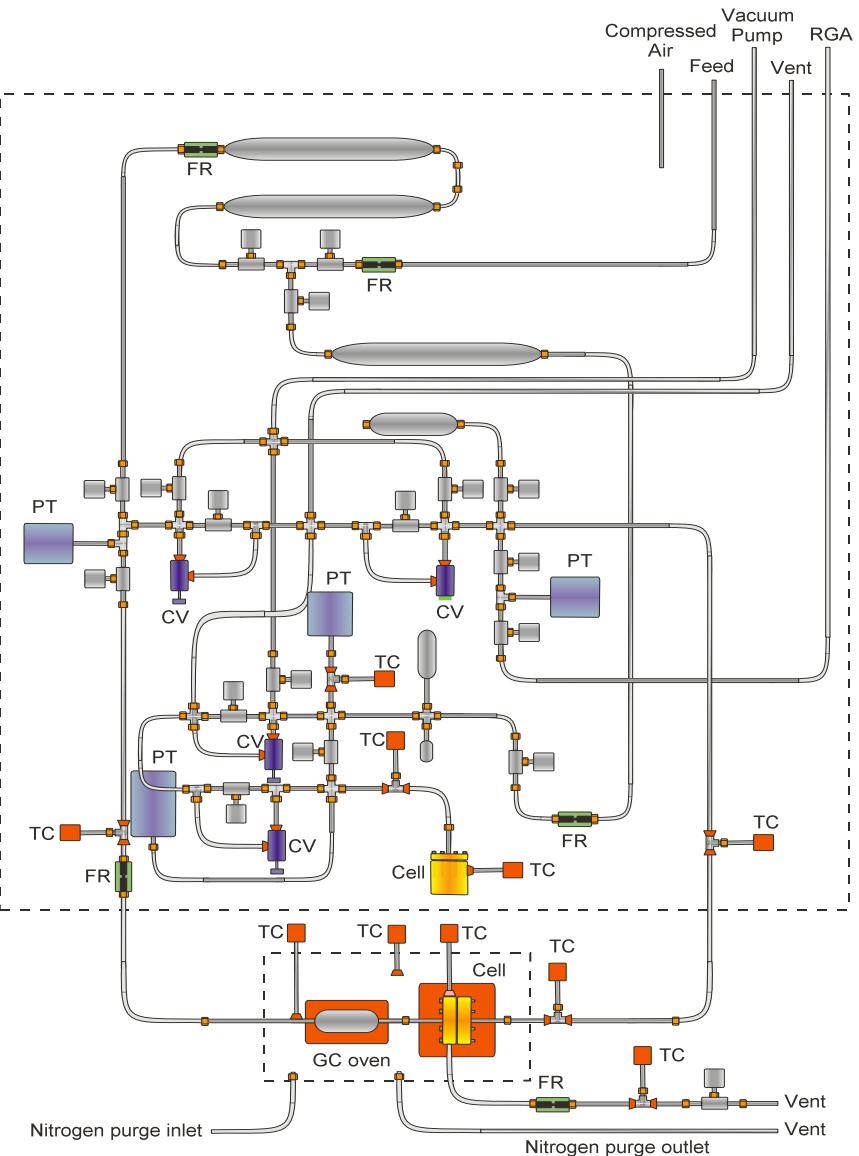
- cells
- reservoirs
- pressure transducers (PT)
- thermocouples (TC)

Safety components incorporated in design:

- check valves (CV)
- flow restrictors (FR)
- nitrogen purge

Permeability and solubility cells have their own heaters

Permeation and solubility experiments can be performed simultaneously and independently



High Temperature-High Pressure Permeameter/Gas Solubility Apparatus



USB data acquisition units provide a fast and easy-to-configure interface

In-line thermocouples provide accurate and fast measurements of gas and cell temperatures

Maximum operating conditions: 65 atm, 400 °C (components operate up to 65 °C)
Gas solubility in polymers determined by pressure decay-dual cell method

Results to Date

- **Synthesized high performance polymers capable of withstanding high temperature environments**
- **Synthesized ZIFs and related frameworks**
- **Prepared and characterized MMMs for H₂ separations at 35 °C and 3 atm**
- **Constructed a high temperature-high pressure permeameter - currently in shake-down mode**

Future Work

- Continue synthesis of high performance polymers
- Continue synthesis of ZIFs and related frameworks
- Prepare and characterize MMMs for H₂ separations at NETL test protocol conditions

Membrane Team

ZIF-containing MMMs offer exciting opportunities in hydrogen separations



Postdocs

Dr. Grace Kalaw
Dr. Edson Perez

Graduate students

Jing Liu
Josephine Ordoñez
Sumudu Wijenayake
Zhen Zhang

Undergraduate students

Mishelle Kochumottom
Pauras Memon
Kelsey Musselman
Saskia Versteeg

